

Environmental Impact of Cadmium: A Review by the Panel on Hazardous Trace Substances

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Introductory Note

This report is the result of a review by a Panel on Hazardous Trace Substances, as part of a report to an *ad hoc* Committee on Environmental Health Research whose chairman was Dr. David Rall, Director of the National Institute of Environmental Health Sciences, NIH.

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The Panel undertook as one of its charges an in-depth examination of several groups of chemicals. This examination was aimed at defining sources of environmental contamination by these chemicals, their distribution in the environment, their transport and alteration, and their biological effects on humans and on other components of the biosphere.

The Panel has also taken the view that it will be important to develop quantitative means for understanding the patterns of the movement of these materials into, and their alteration and persistence within the biosphere; tentative models aimed at these objectives have been developed.

The first report by the Subpanel on polychlorinated biphenyls has been published (1). The present report on Cadmium is an extensive review of this element, prepared by the Subpanel on Cadmium, identified above. It has been reviewed in detail both by the Subpanel and by the entire Panel on

Hazardous Trace Substances. A number of suggestions that emerged from this review have been incorporated into the report. To this extent, the report is a collective effort. However, the chapters or parts of chapters were each the direct responsibility of one or more authors.

The sections on General Properties and Uses and Environmental Forms and Sources were contributed primarily by M. Fleischer; the section on Cadmium Material Flows was contributed primarily by A. F. Sarofim; the section on Effects on Man and Animals was prepared mainly by D. W. Fassett and P. B. Hammond; the sections on Cadmium in Plants and Animals and Ecological Effects were contributed by H. T. Shacklette and I. C. T. Nisbet; The section on Analysis for Traces of Cadmium was prepared by S. Epstein and M. Fleischer. In addition, we are deeply indebted to many colleagues who contributed valuable advice and suggestions.

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General Summary

Cadmium was recognized many years ago to be a highly toxic element, and the need for precautions in industrial operations in which workers were exposed to dusts and vapors of the element or its compounds had long been known. It was not, however, until comparatively recently that concern began to be expressed over the possible effects on human health of exposure over long periods to low concentrations of cadmium, in part because of its steadily increasing consumption and consequent increase in the general environment, and in part because of the outbreak of the itai-itai disease in Japan in the late 1940's and early 1950's. Exposure to cadmium, originating from smelter wastes and concentrated by the rice plant to levels far above those of the normal environment, has been shown to have been one of the causative factors in this disease.

The present report reviews and assesses the information available to November 1972 on the environmental occurrence, transport, and biological effects of cadmium with special attention to significant gaps in our knowledge, and recommends areas of research for future studies.

Occurrence, Transport, and Biological Effects

Cadmium is a relatively rare element that is rather uniformly distributed in the most abundant rocks of the Earth's crust, which has an average content of 0.15–0.2 ppm Cd. It is slightly concentrated in shales, especially in those rich in organic matter, in lacustrine and oceanic sediments, in manganese nodules, and in marine phosphorites; the latter average about 25 ppm Cd. The only natural concentrations of commercial interest are those in sulfide deposits, especially those containing zinc, lead, and copper, from which it is recovered as a by-product. Total production in the United States and in the world reached all-time highs in 1969 of 5,736 and 17,576 metric tons, respectively. Production decreased in 1970 and 1971, but it has been estimated that consumption in the United States will nearly double by the year 2000 to a level of about 13,600 metric tons.

Cadmium metal has an appreciable vapor pressure, higher than that of zinc, at the temperatures used in smelting ores, in the manufacture of metallic alloys, and in the reprocessing of cadmium-containing alloys and of cadmium-plated materials. These processes account for about 90% of the cadmium of atmospheric emissions, estimated by Davis et al. (2) to be about 2300 metric tons annually in the United States. The only other major sources of atmospheric emissions of cadmium are the burning of coal and oil, the burning of cadmium-weighted plastics, and the burning of sewage sludge. This estimate of total emission of cadmium to the atmosphere is in qualitative accord with published measurements of the cadmium content of the air in various parts of the United States, although data on

residence time in the atmosphere are very scanty. The data on the contents of cadmium in soils near point sources of cadmium emissions, such as smelters and metallurgical plants, show that the fall-out has resulted in high concentrations of cadmium close to those sources.

Most fresh waters contain less than 1 $\mu\text{g/l}$ Cd; sea water averages about 0.15. Data on the transport of cadmium in aqueous systems are too fragmentary to permit reliable balances of the flow of cadmium to be constructed, but they suggest that erosion and weathering of rocks and soils contribute far less cadmium to streams in the environment than that contributed by man's activities. Sewage sludge contains notable concentrations of cadmium, and the leaching of such sludge that has been used for land fill could contribute appreciable amounts of cadmium to the drainage system. Information is lacking on the behavior in soil and in drainage systems of the appreciable amounts of cadmium added to the soil in superphosphate fertilizers.

Plants exposed to concentrations of cadmium above those of normal background contain higher than normal concentrations of cadmium. Mosses appear to be especially good indicators of exposure to high concentrations. Damage to plants from excess cadmium has been reported, but the concentrations of cadmium required were higher than even those in soils of contaminated areas.

Only scattered data are available on levels of cadmium content in wild or domestic animals. The levels found in animals are generally much lower than those found in adult humans. No clear geographical correlation has been demonstrated between levels in herbivorous animals and levels in vegetation. In marine animals, the highest concentrations recorded have been in pelagic zooplankton (13 ppm, dry weight), molluscs (locally up to 73 ppm, wet weight), and plankton-eating birds (20–53 ppm, wet weight, in livers). There is no evidence that cadmium concentrates in marine food chains. Adverse effects on reproduction of fish have

been reported at concentrations of cadmium similar to those of moderately polluted waters.

The average intake of cadmium by humans is generally estimated to be about 20–50 $\mu\text{g/day}$, mostly from food. Intestinal absorption is low, probably about 3–8%; the cadmium is notably concentrated in the kidneys and liver, which contain 50–75% of the total body burden. A higher proportion of the cadmium reaching the respiratory tract is absorbed, but the total amount so absorbed is less than that from foods, except perhaps for smokers. The high content of cadmium reported for tobacco may cause smokers to have considerably higher body burdens of cadmium than nonsmokers. The total burden of cadmium in humans increases with age from very little at birth to an average of about 30 mg in the age range 40–50; it may decrease slightly after that.

Exposure to fumes or dusts of cadmium metal or cadmium oxide is known to cause acute pulmonary edema. Chronic exposure to cadmium through the respiratory tract produces a number of toxic effects, the most important of which is chronic emphysema, accompanied by renal disturbance. The effects noted in the itai-itai disease in Japan differ in many respects from the foregoing. The victims were almost all women over 50 who had borne several children; the disease was characterized by osteomalacia and osteoporosis, as well as renal damage. Although cadmium has been implicated as a causative agent, it seems probable that there was profound disturbance of calcium metabolism and that deficiencies of calcium, vitamin A, and vitamin D played important roles in the disease.

It has repeatedly been suggested that build-up of cadmium in the body (or perhaps an increase of the ratio cadmium/zinc) is related to the occurrence of hypertension in man. Experimental studies of rats and rabbits indicate that these animals develop hypertension after intake of cadmium orally or by injection. However, epidemiological studies of persons occupationally exposed to

cadmium and post-mortem studies of cadmium levels in the kidney have not yielded unequivocal statistical evidence of a relation between cadmium content or cadmium/zinc ratio and hypertension.

Carcinogenic effects of cadmium have not been recognized in humans.

In summary, cadmium has not yet been proved to be a hazard to the average individual exposed to the average levels now present in the environment. The data from Japan, however, strongly suggest that part of the population is more sensitive to these hazards because of dietary deficiencies. Further research is needed on the hazards of average levels of cadmium to such individuals and on the hazards due to higher than average intakes of cadmium by persons who live in areas of high emission, who are heavy smokers, or who eat much shellfish. In the meantime, precautions are necessary to decrease emissions from the major sources and to insure that present levels of cadmium in the environment are not increased.

General Recommendations

One of the major purposes of this review was to identify gaps in our knowledge of the impact of cadmium in the environment and to suggest researches aimed at filling such gaps. Specific recommendations are made at the end of each chapter of this report. More generally, however, the Subpanel has found, as have other groups that have made similar reviews, that assessments of this kind are greatly hampered by a notable lack of interdisciplinary coordination of research on environmental pollutants. This is, of course, a natural consequence of the fact that so many disciplines and special fields of research, commonly with very limited contact with one another, are involved in such research, thus greatly increasing the difficulty of assembling the results into a coherent picture.

The Subpanel concurs with the Subpanel on Polychlorinated Biphenyls that there is a need for the development of general systems models to describe the transport of environmental pollutants. It proved to be

difficult to prepare a model for the transport of cadmium which satisfactorily explained ambient concentrations of cadmium, particularly in surface run-off. However, new technological developments—such as the large increase in recent years of the production of cadmium-weighted plastics—emphasize the need for generalized models applicable to a variety of substances, yet flexible enough to meet changing conditions.

Our review has also emphasized the need to study environmental problems as a whole, rather than in piecemeal fashion. Thus, the effects of emissions from metal smelters, a major source of emissions of cadmium, are the sum of the effects due not only to cadmium, but also to zinc, lead, arsenic, and sulfur dioxide, and possibly also to other elements such as copper and thallium, so that conclusions based on the study of a single element must be extremely uncertain. It is therefore important that such problem be considered as a whole, not only in systems models, but also in generalizing monitoring systems and in designing experiments.

As with the PCB problem, a major gap in our understanding of the cadmium problem is that we do not know how to apply data from laboratory studies on the toxicity of cadmium to its effects on animal populations in the natural environment. The difficulty of showing that adverse effects are occurring in the field indicates the need for fuller studies of the effects of environmental contaminants on animal communities, both in model ecosystems (microcosms) in the laboratory and in real ecosystems in the field. Similar difficulties in evaluating the consequences of low-level exposure of humans over long periods of time emphasize the urgent need for improved epidemiological studies of these effects.

General Properties and Uses

Chemical, Physical, and Geochemical Properties

Cadmium is a chemical element, atomic number 48, atomic weight 112.40, consisting

of eight stable isotopes of abundance: ^{106}Cd , 1.22%; ^{108}Cd , 0.88%; ^{110}Cd , 12.39%; ^{111}Cd , 12.75%; ^{112}Cd , 24.07%; ^{113}Cd , 12.26%; ^{114}Cd , 28.86%; ^{116}Cd , 7.58%. Like zinc and mercury, cadmium is a transition metal in Group IIb of the periodic table of elements. Cadmium and zinc, however, differ from mercury in that the latter has 14 additional electrons in the fourth orbital, which probably accounts for the high stability of compounds with mercury-carbon bonds, whereas the similar alkyl-cadmium compounds are extremely unstable, reacting rapidly with water and moist air under environmental conditions. Unlike mercury, cadmium and zinc show only valence + 2 in their compounds; they are also generally similar in reactivity, zinc being the more reactive, and cadmium showing a slightly greater tendency to form covalent bonds, especially with sulfur.

The ionic radius of cadmium is 0.88 Å for fourfold coordination, 1.03 Å for sixfold coordination. The sulfide, CdS (dimorphous, like the corresponding zinc and mercury sulfides), and the carbonate, CdCO_3 , are less soluble than the corresponding zinc compounds, but the hydroxide, $\text{Cd}(\text{OH})_2$, is more soluble than $\text{Zn}(\text{OH})_2$. Cadmium forms a wide variety of soluble complexes, notably with cyanides and amines.

Cadmium metal is a bluish-white to silver-white metal, density 8.645, Brinell hardness 21, that melts at 321°C and boils at 765°C . Its vapor pressure, greater than that of zinc, is 1.4 mm at 400°C and 16 mm at 500°C , so that losses by vaporization are to be expected during metallurgical processing. The vapor is very reactive, quickly forming finely divided CdO in the air.

The geochemistry of cadmium has been reviewed by Ivanov (9) and by Wakita and Schmitt (4). It is a strongly chalcophilic element, i.e., it is concentrated in sulfide deposits, in which it follows zinc and mercury, and to a much lesser extent lead and copper. The abundance of cadmium in the Earth's crust is generally estimated to be 0.15–0.2 ppm. Its concentration is low in all igneous rocks and its content in them shows no clear relations to those of any

major element, nor to that of zinc, the ratio Zn/Cd varying widely in all types of igneous rocks. Higher concentrations of cadmium occur in shales, oceanic and lacustrine sediments, phosphorites, and oceanic manganese nodules; in these the ratio Zn/Cd is generally lower than in igneous rocks.

Use Patterns of Cadmium

The principal uses of cadmium are as alloys, in plating metals, pigments, as a stabilizing material for polyvinyl plastics, and in batteries. Two different estimates of the material flow of cadmium in the USA in 1968 are shown in Figures 1 and 2, as given by Davis et al. (2) and by Heindl (5). The values for miscellaneous or other uses (Fig. 1) include uses in fungicides, nuclear control rods, phosphors, ceramics, and others.

Data from the U. S. Bureau of Mines (6) on U. S. and world production of cadmium are summarized in Table 1. Consumption in the United States was in metric tons 6046 in 1968, 6845 in 1969, with a sharp decrease to 4218 in 1970. It has been estimated that U. S. annual consumption will rise to about 13,600 metric tons by the year 2000.

Environmental Forms and Sources

Mineralogy

The mineralogy of cadmium has been reviewed by Vorob'eva (7). Only a few cadmium minerals are known: greenockite, hexagonal CdS ; hawleyite, cubic CdS ; cadmoselite, hexagonal CdSe ; montepionite, CdO ; otavite, CdCO_3 , and cubic cadmian metacinnabar (saukovite), $(\text{Hg}, \text{Cd})\text{S}$ with Cd 11.7%. All of these except greenockite are very rare, and they are all of secondary origin, except possibly some greenockite.

Nearly all the cadmium in primary sulfide ores occurs as a minor element in sulfides of other elements, especially those that have fourfold covalent bonding. Cadmium occurs mainly in the zinc sulfides sphalerite and wurtzite, the maximum cadmium content of sphalerite being about 5%, and the entire series wurtzite-greenockite being known.

C A D M I U M
MATERIAL FLOW CHART-1968
(THOUSAND POUNDS)

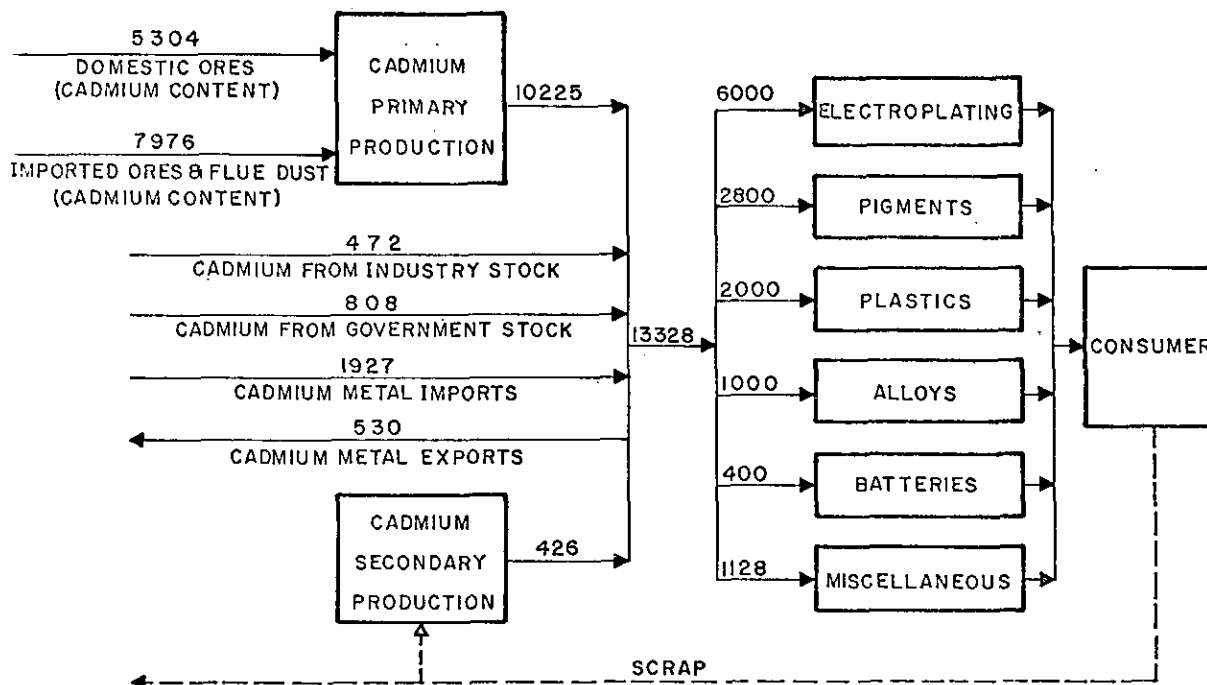


FIGURE 1. Cadmium material flow chart, 1968 (thousands of pounds). Data of Davis et al.(2).

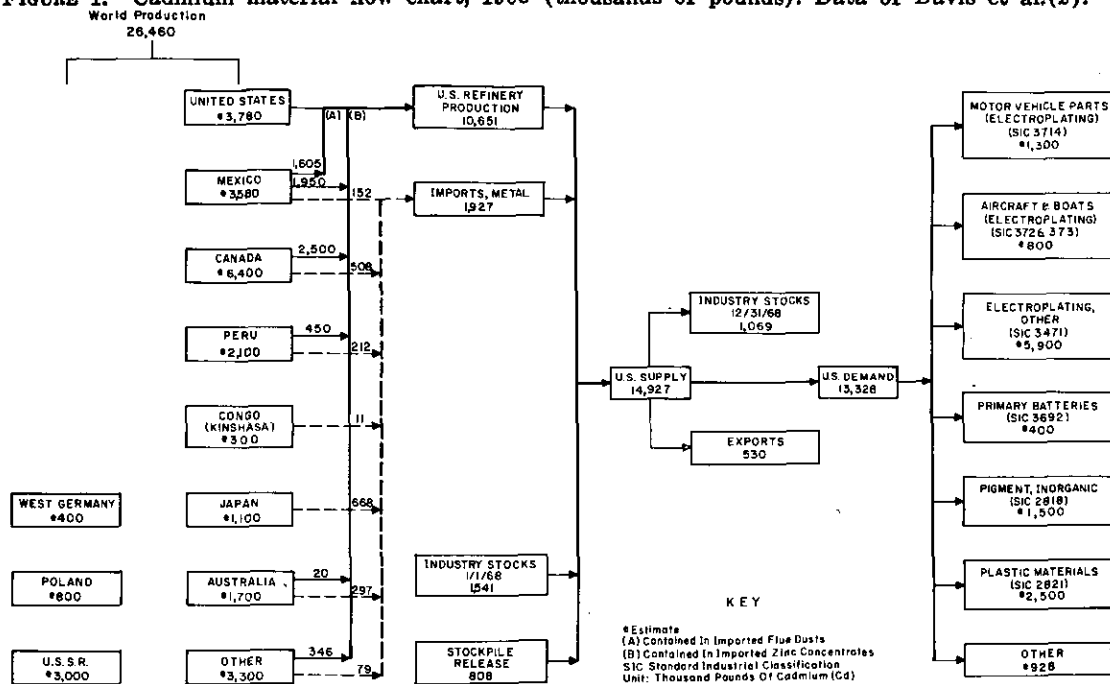


FIGURE 2. Supply-demand relationships for cadmium, 1968. Data of Heindl (5).

Table 1. World and U.S. production of zinc and cadmium.*

Year	Metric tons			
	Cd (U.S.)	Cd (world)	Zn (U.S.)	Zn (world)
1971	3,597	15,490	554,000	6,700,000
1970	4,293	16,620	1,053,000	6,680,000
1969	5,736	17,576	1,215,000	6,494,000
1968	4,831	14,674	1,213,000	6,044,000
1967	3,946	13,186	1,116,000	5,876,000
1966	4,745	13,023	1,222,000	5,448,000
1965	4,386	11,676	1,188,000	5,227,000
1964	4,744	12,674	1,131,000	4,872,000
1963	4,491	11,894	1,050,000	4,464,000
1962	5,052	11,903	1,034,000	4,332,000
1961	4,725	11,295	995,000	4,101,000
1960	4,738	11,113	957,000	3,957,000
1955-1959 (avg)	4,487	9,435	1,064,000	3,753,000
1946-1950 (avg)	3,644	4,980	940,000	2,260,000

* Data recalculated from U.S. Bureau of Mines *Mineral Yearbook* (6).

The average cadmium content of zinc sulfides of individual deposits ranges from 0.02 to 1.4%, with a median content about 0.3% Cd. Fourteen other sulfides have been reported to contain more than 500 ppm Cd; the most important of these, with maximum and median reported contents of cadmium respectively, are: galena, PbS, 5000, 10 ppm; tetrahedrite-tennantite, $(\text{Cu}, \text{Zn})_2(\text{Sb}, \text{As})_4\text{S}_{13}$, 2400, 600 ppm; metacinnabar, HgS, 11.7%, <10 ppm; chalcopyrite, CuFeS_2 , 600, <10 ppm.

Cadmium is readily dissolved from sulfides by acid waters formed during the oxidation of sulfide ores. Such mine waters have been reported to contain up to 42 ppm Cd, although values of 0.1-2 ppm are much more common. The subsequent fate of the dissolved cadmium depends largely on Eh-pH conditions and on the type of country rock encountered by the solutions, but much if not most of the cadmium appears to be precipitated before travelling very far. The precipitates generally have lower Zn/Cd ratios than the primary sulfides of the same deposits, that is, they are enriched in cadmium. This is true of secondary sulfides (sphalerite-hawleyite series, wurtzite-greenockite series), the zinc carbonate smithsonite (maximum Cd, 0.87%), the zinc silicate hemimorphite (maximum Cd, 1.2%), the basic iron sulfate jarosite (maximum

Cd, 1.0%), and iron oxides (maximum Cd, >0.1%). The possibility of pollution of natural waters by cadmium dissolved from sulfide ores is discussed in a later section.

The zinc silicates genthelvite, $(\text{Zn}, \text{Fe}, \text{Mn})_3\text{Be}_3(\text{SiO}_4)_3\text{S}$, and willemite, Zn_2SiO_4 , have been reported to contain up to 450 and 120 ppm Cd, respectively.

Cadmium in Igneous and Metamorphic Rocks

Relatively few analyses of igneous rocks for cadmium are available; these are summarized in Table 2. The range reported is <0.001 to 1.6 ppm, with very few analyses above 0.5 ppm; alkalic rocks, alkalic granites, and rhyolites have cadmium contents slightly above average. Vincent and Bilefield (8) found a distinct, but slight enrichment in cadmium with increasing magmatic differentiation. The ratio Zn/Cd varies widely in all types of rocks, with recorded extremes of 27 to 7000; no clear variation of cadmium content with any major constituent is apparent.

Few determinations have been made of the distribution of cadmium among coexisting minerals of igneous rocks. In three gabbroic rocks analyzed by Nesterenko et al. (10), cadmium was present in all the rock-forming minerals, in amounts of 0.015-0.10 ppm, most of it being present in olivine and pyroxene.

Table 2. Cadmium in igneous rocks.

Type of rock	No. of samples analyzed	Cadmium content, ppm		Ratio Zn/Cd
		Range	Average	
Rhyolitic	43	0.03-0.57	0.23	480-177
Granitic	43	0.01-1.6	0.2 ^a	90-7000
Intermediate	4	0.017-0.32	—	—
Basalts, diabases, gabbros	79	0.01-1.00	0.13	80-3600
Peridotite	3	<0.001-0.029	0.03	—
Dunite	1	0.005-0.154	—	—
Eclogites	4	0.03-1.6	0.1	—
Alkalic rocks	7	0.04-0.90	0.25	27-1430

^a Marowsky and Wedepohl (9) give 0.075-0.1 ppm.

Marowsky and Wedepohl (9) found that regional metamorphism has reduced the cadmium content of metamorphosed shales of the Swiss Alps by at least one order of magnitude.

Cadmium in Sedimentary Rocks

The available data are summarized in Table 3. The content of cadmium is apparently low in limestones and sandstones, but cadmium is appreciably concentrated in shales, oceanic, and lacustrine sediments, oceanic manganese oxide nodules, and in phosphorites. Of special interest are the data of Tourtelot et al. (11), which indicate that cadmium, like mercury, is especially concentrated in shales with high content of organic matter. Gulbrandsen (12) states that cadmium and zinc in the phosphorites of the Phosphoria formation are associated with organic matter.

This association of cadmium with organic matter plus the known existence of organic compounds of cadmium, such as dimethylcadmium and diethylcadmium, raises the specter that cadmium, like mercury, might be recycled geochemically in such a form. However, Fassett (13) has pointed out that such compounds are much less stable than the analogous mercury compounds. It would be highly desirable to have further study of this possibility.

Cadmium in Coal and Oil

Data on the cadmium content of coal and oil are scanty. Lagerwerff and Specht (15) found 1-2 ppm Cd in eight bituminous coals from Kentucky and Illinois. Abernathy et al. (16) found cadmium in only 70 of 827 coal samples from the U.S. in amounts of 2-100 ppm Cd in ash (approximately 0.2-10 ppm Cd in the coal). These

Table 3. Cadmium in sedimentary rocks.

Rocks	No. of samples	Cadmium content, ppm		Median
		Range	Average	
Limestones	23	—	0.10	—
Sandstones (composite of 14)	—	—	<0.03	—
Shales	103	<0.3-11.0	1.4 ^a	0.8
Org. C <0.5%	}	<0.3-0.8	0.35	0.3
Org. C 0.5-1.0%		0.3-1.8	0.8	0.7-0.8
Org. C >1%		0.5-8.4	2.0	1.2
Oceanic sediments	189	0.04-1.88	0.5 ^b	—
Lake sediments	26	5-19	11.	—
Oceanic Mn oxides	34	<3-21.2	8	5.3
Phosphorites	163	<10-500	25	—

^a Marowsky and Wedepohl (9) give 0.3 ppm.

^b Aston et al. (14) recently reported 0.04-0.58 ppm, avg. 0.226 ppm, in 35 Atlantic deep-sea sediments.

figures can be checked in a rough way by examining the hundreds of available analyses for Zn in U.S. coals. They range from 7.6 to 108 ppm Zn; assuming a ratio Zn/Cd = 100, this gives about 0.08 to 11 ppm Cd; assuming a ratio Zn/Cd = 200, 0.04–5.4 ppm Cd.

Much higher amounts of cadmium have been reported in peat collected from bogs in mineralized areas in Finland (17) and at Manning, N.Y. (18). The latter found 0.37–190, median 3.0 ppm Cd, in 124 samples of peat (dry weight).

Data on crude oils by Israelyan (19) and by Porfir'ev et al. (20) indicate ranges of cadmium content 0.16 to 16 ppm. Bertine and Goldberg (21) estimate an average content of 0.01 ppm Cd in oil. Lagerwerff and Specht (15, 22) found 0.42–0.53 ppm Cd in three heating oils, 0.07–0.10 ppm in three diesel oils, and 0.20–0.26 ppm in three motor lubricating oils; Davis (2) states that five samples of motor lubricating oil contained an average of 0.48 ppm Cd; Creason et al. (23) report 0.24–0.66 ppm Cd in motor oil. The cadmium content of these motor oils is at least partly due to the use of zinc dithiophosphate as an additive.

Cadmium in Air

Data on the concentration of cadmium in air of the United States, collected by the National Air Sampling Network, have been summarized by Tabor and Warren (24), Athanassiadis (25), and by Schroeder (26). Schroeder, considering the data collected through 1966 for 58 cities and 29 nonurban areas, gives ranges of concentration [ng Cd/m³; 1 nanogram (ng) = 10⁻⁹]: 2–370 for urban areas, 0.4–26 for nonurban areas. Kneip et al. (27) reported measurements in 1968: Bronx, New York City 6–22, average 14; lower Manhattan, New York City 9–36, average 23; Tuxedo, N. Y. (nonurban) 1–5, average 3. Lee et al. (28) reported an average of 80 for downtown Cincinnati, Ohio, 20 for Fairfax, Ohio (suburban). Harrison (29) found an average of 19 for the Chicago area. Friberg et al. (30) quote weekly means of 5 in the center of Stock-

holm and a monthly mean of 0.9 in a rural area in Sweden, also 1.5 in Erlangen, Germany. Just and Kelus (31) reported 2–51 in the air of 10 Polish towns in 1967. Dudley et al. (32) found 3–8.7 in five marine aerosols.

All these data emphasize the probability that nearly all airborne cadmium is due to man's activities. The highest concentrations are reported from cities with considerable industry, especially metallurgical and smelting operations. Towns in the United States reporting maximum Cd values ≥ 100 ng/m³ are given in Table 4.

Friberg et al. (30) quote weekly means of 500 ng Cd/m³ at a distance of 100 m and 200 ng/m³ at a distance of 400 m from a Japanese smelter, and 160–320 ng/m³ at a distance of 500 m from another Japanese smelter. Weekly means of 600 (maximum 54000) ng/m³ at a distance of 100 m and of 300 at a distance of 500 m were recorded in Sweden near a factory using copper-cadmium alloys. These are several hundreds times as great as concentrations in uncontaminated areas.

Measurements of monthly deposition of cadmium at various distance from factories are quoted by Friberg et al. (30) (mg Cd/m² per month); Sweden, 100 m, 4–40; 500 m, 0.5–3.0; 1000 m, 0.4–4.0; Japan, 500 m, 6.2; 1400 m, 1.8. Greszta and Godzik (34) found 40–70 at a distance of 800 m from a Polish zinc metallurgical works. Additional data are given in the sections Cadmium in Soils and Cadmium in Plants.

Data are not yet available on the fate of air-borne cadmium and its residence time in the atmosphere. It is presumed to be carried down by rain and snow, but the few determinations made so far are inadequate. The data of Lagerwerff (35) indicate that near highways nearly half the cadmium taken up by plants is from airborne sources.

Cadmium in Atmospheric Emissions

The recent estimates by Davis et al. (2) are summarized in Table 5. It should be noted that these are not based on actual

Table 4. Maximum Cd above 100 ng/m³ in air of U.S. cities.

State	City	Year	Maximum Cd content, ng Cd/m ³	Reference
Arizona	Tucson	1960	140	(25)
Colorado	Denver	1962	310	(25)
Illinois	Chicago	1960	400	(25)
Illinois	E. St. Louis	1963	180	(25)
Indiana	Gary	1960	110	(25)
Indiana	Indianapolis	1960	100	(25)
Louisiana	Baton Rouge	1970	290	(33)
Maryland	Baltimore	1964	110	(25)
Michigan	Calumet (near)	1969	350	(29)
Missouri	St. Louis	1962	420	(25)
Missouri	St. Louis	1964	290	(25)
Nebraska	Omaha	1961	110	(25)
New Jersey	Newark	1964	350	(25)
New York	New York City	1961	210	(25)
Ohio	Akron	1960	130	(25)
Ohio	Cincinnati	1964	110	(25)
Ohio	Columbus	1961	110	(25)
Ohio	Marietta	1969	128	(29)
Ohio	Youngstown	1960	140	(25)
Pennsylvania	Allentown	1961	330	(25)
Pennsylvania	Bethlehem	1961	140	(25)
Pennsylvania	Philadelphia	1961	290	(25)
Texas	El Paso	1962	310	(25)
Washington	Tacoma	1954-1959	170	(25)
West Virginia	Charleston	1961	160	(25)

measurements, but are calculated from production data plus assumptions as to the losses of cadmium in each type of operation.

The emissions in smelting operations are undoubtedly considerable (see above), yet the figure in Table 5 for emissions from this source is nearly 20% of the total production of the United States in 1968 (Table 1), which seems high. The emissions from reclamation of steel and radiator scrap assume that all of the cadmium in these materials, none of which is recovered, reaches the atmosphere. The emissions from burning cadmium-stabilized plastics were calculated on the assumptions that 40% of the plastic went to waste, that 15% of the waste was burned, and that all of the cadmium in burned material reached the atmosphere. It seems likely that these estimates are somewhat high.

On the other hand, Table 5 does not include estimates of possible cadmium emissions from the burning of coal and heating oil; these might amount, respectively, to 100

tons and 30 tons/yr (2); Bertine and Goldberg (21) estimate about 2.2 tons/yr from burning oil.

If cadmium were present in appreciable amounts in gasoline, the emission from this source could be serious. Reports of its presence in gasoline have been published (36, 37), but these have not been verified. Lagerwerff and Specht (15, 22) reported finding 6 parts per billion (ppb) Cd in one of 12 gasolines tested, the rest containing less than 0.01 ppb.

Cadmium in Soils

A selection of representative data on the cadmium content of soils is given in Table 6. Recent analyses of uncontaminated soils indicate that normal contents of cadmium are less than 1 ppm, perhaps about 0.4 ppm on the average. A few analyses that show considerably higher values are unexplained; Malyuga (38) reported 16 and 45 ppm in chernozems developed on serpentinite, USSR;

Table 5. Estimates of atmospheric emissions of Cd in the U.S. for 1968.*

	Cd, lb $\times 10^{-3}$
Processing	
Mining and ore processing	0.53
Smelting	2100.
Reprocessing of metals	33.53
Electroplating	Very low
Pigment manufacture	21.
Plastic manufacture	6.
Alloys	5.
Battery manufacture	0.40
Miscellaneous	1.13
Consumptive uses	
Wear of automobile tires	11.4
Burning of oil, motor vehicles	1.82
Fungicide use	0.5
Fertilizers (superphosphate)	0.91
Steel scrap reclamation	2000.
Radiator scrap reclamation	250.
Plastic and pigment incineration	190.
	4622.22 (=2300 tons)

* Data of Davis et al. (2).

Krupenikov et al. (39) found 3–30 ppm in soils from Moldavia.

Many more analyses of contaminated soils are given in the references cited in that section of Table 6 and by Burkitt et al. (40). The data of Lagerwerff and Specht (15) and of Lagerwerff (35) show clearly the extent of soil contamination near highways. Contamination from emissions from smelters and metallurgical plants is even more striking. The data of Miesch and Huffman (41) show that the effects of contamination from a smelter that had been operating for 80 years were discernible at distances of at least 11 miles away, and probably further, as shown in Figures 3 and 4.

Cadmium is evidently mobile in these smelter-contaminated soils and works its way downward to a depth of at least 30 cm, as illustrated by the data of Kobayashi (42), which show at 5 cm, 44 ppm Cd; at 10 cm,

32 ppm; at 20 cm, 6.9 ppm; at 30 cm, 1.4 ppm; at 40 cm, 0.4 ppm Cd.

Table 6 gives means of concentrations of cadmium in soils of varying environments in the area of Grand Rapids, Michigan (43). The contents are significantly higher in the industrial and airport zones than in the residential.

Considerable amounts of cadmium may be added to soils by the addition of phosphate fertilizers or by the application of sewage sludge.

Cadmium in Waters

Determinations of cadmium in waters are summarized in Table 7. Most of the analyses of sea water are in the range 0.05–0.2,

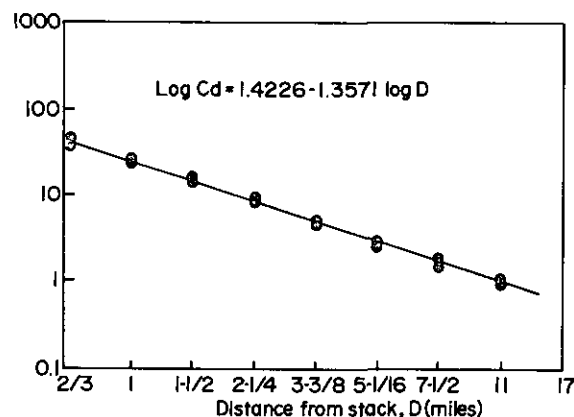


FIGURE 3. Cadmium contents of soil samples at depths 0–4 in. as a function of distance from smelter stack. Data of Miesch and Huffman (41).

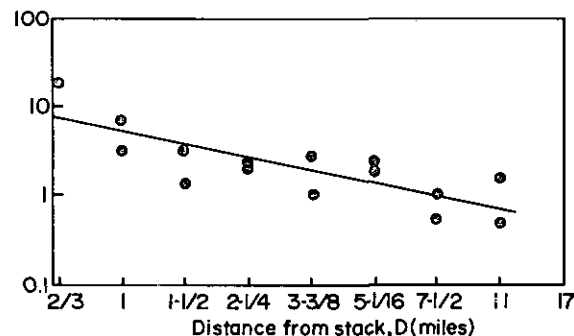


FIGURE 4. Cadmium contents of soil samples at depths 6–10 in. as a function of distance from smelter stack. Data of Miesch and Huffman (41).

Table 6. Cadmium in soils.

No. of samples	Depth, cm	Locality and type of soils	Cd content, ppm		Ref.
			Range	Average	
Normal Soils					
40	A, B, and C horizons	USSR, tundra, podzols, forest, red earth	0.01-0.07	0.06	(44)
33	0-20	Poland, distant from industrial areas	max. 0.04	0.016	(45)
—	—	Wales, Ystwyth Valley gley	—	1.0	(46) *
4	10-15	32 m from highways, Md., Mo., Ohio ^b	0.12-0.52	0.26	(22) *
17	6-10	Helena Valley, Montana 11-38 mi from smelter	<0.5 -2 *	1.4 *	(41) *
2	40-60	Annaka City, Japan 900 m from refinery	0.3 -0.4	0.35	(42) *
4	—	S. W. Wales	0.3 -0.5	0.4	(47) *
33	Surface	Lower Fraser Valley, Brit. Columbia	—	0.88	(48) **,d
Contaminated Soils					
67	0-20	Poland, industrial areas	max. 0.3-0.8	0.17-0.28	(45)
—	—	Wales, Ystwyth Valley contaminated	1.5 -3.0	—	(46) *
4	0.5	8 mi from highways, Md., Mo., Ohio ^b	0.90-1.82	1.28	(22) *
7	0.10	Helena Valley, Montana 2/3 mi from smelter	26-160	72	(41) *
—	Surface	Annaka City, Japan, 150-250 m from smelter	23- 38	—	(42) *
—	5	Annaka City, Japan, 900 m from smelter	44	—	(42) *
1	0-10	Poland, 600 m from zinc metallurgical factory	250	—	(34)
1	15-30	zinc metallurgical factory	110	—	(34)
—	—	S. W. Wales, Swansea, 1.5 km from contaminated area	26	—	(47) *
—	12.5-27.5	Bartlesville, Okla., 1500 ft from smelter	450	—	(49)
4	Surface	Brit. Columbia, 15 mi from smelter	7.9 -95.2	49.0	(48) **,d
70	0-5	Grand Rapids area, Mich.	—	—	—
		Residential area	—	0.41	(43)
91	0-5	Agriculture area	—	0.57	(43)
86	0-5	Industrial area	—	0.66	(43)
7	0-5	Airport	—	0.77	(43)

* Atomic absorption spectrometry.

^b Samples collected near U.S. #1, Beltsville, Md.; Washington-Baltimore P'way, Bladensburg, Md.; Interstate #29, Platte City, Mo.; Seymour Rd., Cincinnati, Ohio.

* These values probably reflect some contamination.

^d Cadmium dissolved by 1N HNO₃.

averaging about 0.15 $\mu\text{g/l}$. or about 0.15 ppb. Many of the samples analyzed are near-shore samples and may have been contaminated (56). Thus the recent analyses by Jaakkola et al. (59) are higher than the average; the samples from the Gulf of Bothnia had been contaminated by discharges from a lead-zinc smelter.

Krauskopf (74) has calculated that sea water now contains less than 0.1% of the cadmium that has been supplied by erosion of the land surface and is far below the concentration calculated from solubility data, so that sea water is distinctly undersaturated with respect to cadmium. The data in Tables 3 and 7 indicate that nearly all the cadmium has been removed by coprecipitation with or adsorption on clays, hydrous manganese oxides, and phosphorites. Posselt (75) has shown that the removal of cadmium from waters by precipitation of hydrous oxides of Fe^{3+} and Mn^{4+} is rapid and effective.

Most fresh waters contain less than 1 ppb Cd. The chemistry of cadmium in surface and ground waters has recently been reviewed by Hem (75), who gives calculations of equilibrium solubilities with $\text{Cd}(\text{OH})_2$ or CdCO_3 , showing minimum solubility at pH 9.0–10.0. Most natural waters were unsaturated with respect to the hydroxide or carbonate; about 20% of the waters had cadmium contents in reasonable agreement with values calculated assuming CdCO_3 as equilibrium solid phase.

Durum et al. (63) found less than 1 ppb Cd in 54% of the 727 surface waters analyzed, which had been filtered through 0.45 μ openings. They did not determine cadmium present in suspension, but Kopp and Kroner (64), who reported finding no cadmium in 97.5% of the 1577 surface waters analyzed, also reported finding no cadmium in suspension in their samples; their spectrographic method, however, was not very sensitive. Friberg et al. (30) point out the need to determine the cadmium content of the suspended matter; they report that 500 m downstream from a cadmium-emitting factory in Sweden, the water contained 4 ppb Cd, the mud 80 ppm Cd (dry weight).

A recent study by Perhac (67), who made ultracentrifuge separations of coarse and colloidal particulate matter from four samples in a mineralized area, showed that the particulate matter had concentrations of cadmium some thousands of times that dissolved in the waters, yet that 85–96% of the total cadmium was present as dissolved material. These data indicate that cadmium is precipitated on stream sediments under some conditions, the extent of precipitation depending on pH, degree of complexing, and many other factors. Abdullah and Royle (72) report that "clean" streams in Wales contain 0.41 $\mu\text{g Cd/l}$.; streams affected by old mining activities contained 1.1–3.4 $\mu\text{g/l}$.

It has been mentioned that mine waters have been reported to contain up to 42 ppm Cd; such waters might reach the drainage system. Mink et al. (77, 78) found traces to 0.45 mg/l. (ca. 450 ppb) Cd in waters of the South Fork of the Coeur d'Alene River, Idaho, corresponding to the transport of up to 394 lb Cd/day. This stream drains an area in which thousands of tons of ground tailings of Pb–Zn–Ag ores were dumped decades ago.

The surface waters that contain more than a few ppb Cd near urban areas have almost certainly been contaminated by industrial wastes from metallurgical plants, plating works, or plants manufacturing cadmium pigments, cadmium-stabilized plastics, or nickel-cadmium batteries, or by effluent from sewage treatment. Few data are available. Tenny and Stanley (79) examined 1123 samples of industrial wastes of the Chicago area and reported that 1.43% contained more than 10 mg/l. Cd, 0.27% contained more than 50 mg/l. Cd; all these were from metal treatment and plating. Among the few well-documented studies of industrial contamination of water supplies by cadmium are those of Lieber and Welsch (80) and Perlmutter and Lieber (81), who traced the spread of cadmium from a plating plant over an area up to 0.8 mile long and 0.2 mile wide, finding ground waters containing up to 3200 ppb Cd.

Table 7. Cadmium in waters.

No. of samples		Cd content $\mu\text{g/L}$ (\sim ppb)			Locality	Method	Reference
Analyzed	Cd not found*	Range	Average	Median			
Sea Water							
1	0	—	0.3	—	Caribbean	Spectrographic	(50)
24	24	<0.7	—	—	Pacific, off Calif.	after concentration	(51)
5	0	0.032-0.075	0.055	—	Irish Sea	Dithizone	(52)
12	0	0.045-0.232	0.166	—	Irish Sea, surface	Dithizone	(53)
—	—	0.6-3.0	1.3	—	Irish Sea and English channel	Polarographic	(54)
3	0	0.081-0.180	0.119	—	English channel	Atomic absorption	(55)
4	—	<0.01-0.38	—	0.06	English channel	Atomic absorption after concentration	(56)
10	—	<0.01-0.52	—	0.11	Irish Sea, western part	Atomic absorption after concentration	(56)
21	—	0.01-0.62	—	0.04	Irish Sea, eastern part	Atomic absorption after concentration	(56)
8	—	<0.01-0.18	—	<0.01	Atlantic, near Scotland	Atomic absorption after concentration	(56)
5	—	<0.01-0.41	—	0.04	Atlantic, NW Ireland	Stripping voltammetry	(57)
4	—	0.29-0.60	—	0.41	North Sea	Atomic absorption	(55)
—	—	—	0.18	—	Atlantic (?)	Atomic absorption after concentration	(58)
5	1	—	0.06	—	Menai Straits	Atomic absorption after concentration	(59)
101	—	0.07-0.71	0.11	—	Atlantic, off coast Africa	Atomic absorption after concentration	(59)
6	—	0.1-2.2	0.7	0.4-0.5	Gulf of Finland	Atomic absorption after concentration	(59)
6	—	0.3-10.2	2.9	0.5-0.6	Gulf of Bothnia	Stripping anodic	(60)
5	—	0.12-0.29	0.19	—	Oslofjord, depth 40 m	voltammetry	(60)
—	—	0.08-0.17	—	—	Coast off Wakayama	Colorimetric after concentration	(61)
—	—	0.1-0.8	—	—	Pref., Japan	Atomic absorption after concentration	(62)
Fresh Waters							
2569	2165	<1-130	—	<1	Surface waters, U.S.	Atomic absorption spectra and spectrographic	(50, 51, 63-67)

3490	3474	<1-207	0.032	—	Surface waters, Siberia	Spectrographic after concentration	(68)
14	12	0-1	—	—	Lake Erie	Atomic absorption spectra	(69)
9	0	0.03-0.15	0.09	—	Lake Ontario	Atomic absorption after concentration	(70)
6	0	0.71-2.08	1.15	—	Linsley Pond, Conn.	X-ray fluorescence	(71)
—	—	—	0.41	—	"Clean" streams, Wales	Atomic absorption after concentration	(72)
167	162	<0.7-71	—	—	Well waters, Calif.	Spectrographic after concentration	(51, 66)
—	—	0.1-1.0	—	—	Hot Springs, Arima, Japan	—	(73)

* The sensitivity is indicated by the figure given as <under range.

Another potential source of cadmium in surface waters is the leaching of land fill or soils to which sewage sludge has been added. Tenny and Stanley (79) reported an average content of 0.003 mg/l. in the final effluent of sewage treatment plants in the Chicago area, nearly all the cadmium having been precipitated in the sludge. Digested sewage from two plants contained 70 and 470 ppm Cd, with total content of 780 lb Cd/day. Similar figures are reported by Regan and Peters (82, 83), who reported a Cd level of 290–2850 mg/l. of total solids in sludges from wastewater treatment plants in Kentucky, and by Berrow and Webber (84), who reported <60–1500 ppm Cd in 42 sewage sludges from England and Wales.

It is likely that cadmium is leached to some extent from dumps containing cadmium alloys or cadmium-stabilized plastics and from soils to which phosphate fertilizers have been added, but no data are available. Horvath et al. (85) found 0.4 $\mu\text{g/l.}$ Cd in South Florida canals draining underdeveloped land 2.8 $\mu\text{g/l.}$ in canals draining agriculturally developed land; the difference is attributed to the addition of the metal in pesticides and fertilizers.

Summary

Cadmium is a relatively rare element; its abundance in the Earth's crust is generally estimated to be 0.15–0.2 ppm. It is not markedly concentrated in any igneous rocks, and its concentration in them shows no clear correlation with that of any major constituent, nor with that of zinc. Higher concentrations of cadmium occur in shales (especially in those rich in organic matter), oceanic and lacustrine sediments, oceanic manganese nodules, and in marine phosphorites; in these ratio Zn/Cd is generally lower than in igneous rocks.

All the cadmium production of the world comes from sulfide ores of zinc, lead, and copper, from which it is recovered as a by-product. Total production in the United States and in the world reached all-time high in 1969 of 5736 and 17,576 metric tons, respectively.

The principal uses of cadmium are in electroplating of metals, in alloys, in pigments, as a stabilizing material for polyvinyl plastics, and in batteries. It has been estimated that consumption in the United States will nearly double by the year 2000 to a level of about 13,600 metric tons.

Data on the cadmium contents of coal and oil are scanty; the range in coal is 0.2–10 ppm; in motor oils, mostly 0.1–0.5 ppm, due at least in part to the addition of zinc dithiophosphate.

Measurable amounts of cadmium are present in the atmosphere. In rural areas the concentration is generally from tenths of a nanogram to 10 ng/m³; in urban areas it is 2–420 ng/m³. Higher values have been reported near smelters and metallurgical plants. Soils near such sources also show much higher concentrations of cadmium than the normal content of about 0.4 ppm.

Recommendations

1. Improvement of our knowledge of the natural transport of cadmium requires better estimates of the distribution of cadmium in igneous and sedimentary rocks and their constituent minerals, and information, now entirely lacking, on the nature of the binding of cadmium in organic-rich shales and in phosphorites.

2. Data are needed on the cadmium content of coal and fuel oil and on the proportion of the cadmium present that reaches the atmosphere during burning, especially from large installations such as power plants.

3. Continued monitoring of the air of our cities is essential, and special studies of the emissions of cadmium by metallurgical plants and zinc smelters should be undertaken.

4. In conjunction with these, study should be made of the fate of atmospheric emissions of cadmium with respect to the time of residence and fall-out with rain or snow, especially in areas of high emission.

5. More data are needed on the emission of cadmium from processes of scrap reclamation and from the disposal of cadmium-weighted plastics.

6. The fate of cadmium in the hydrologic cycle is little known. Studies of the cadmium content of surface waters should be accompanied by study of its content in the associated particulate matter and in stream sediments. Data are needed on the rate of release of cadmium from soils treated with phosphate fertilizers and on the possible leaching of cadmium from galvanized plumbing.

7. Discharges of water from plating works and from plants manufacturing Ni-Cd batteries, Cd pigments, etc., should be monitored carefully.

Cadmium Material Flows

In this section an attempt is made to trace the flow of cadmium from its sources to the areas in which it is accumulated in the environment. The discussion is restricted to fluxes in the U.S. and adjacent seas, but reference is made to European or Japanese studies where these help fill gaps in the picture. Most of the data cited are for the five-year period 1967-1972. Although there is not an exact correspondence in dates of the information drawn from different sources, it is felt that the time span covered is small enough to permit the neglect, for the purposes of formulating gross models of flow, of variations in flow rates and concentration over the period considered.

In view of the near constancy of the ratio of cadmium to zinc in many ores and the similarity in the major uses of the two elements, extensive reference is made to zinc flows and zinc/cadmium ratios. Zinc/cadmium ratios in environmental samples that differ significantly from those in geological reserves are indicative either of errors in sampling and analysis or of selective mechanisms for the flow and accumulation of one of the two metals. Whenever anomalous ratios are encountered, a careful examination of the cause for departure from the norm is warranted.

The section has drawn heavily on the estimates by Davis et al. (2) of atmospheric emissions and on the summary by Chizhikov (86) of cadmium fluxes in smelters and

refiners. Subsequent to preparation of a draft of this section, a very detailed description of the societal flow of cadmium was published by Fulkerson and Goeller (87).

The processing of cadmium will be considered in some detail in order to obtain information on such factors as physical and chemical state that may influence the flow and accumulation of cadmium in the environment. Wherever possible, estimates of emission are tested against measured ambient concentrations.

Mining and Concentration of Ores

Cadmium is recovered with zinc usually from polymetallic ores containing lead and copper. The classification of the ore as zinc, lead-zinc, lead, copper-lead-zinc, or other permutations is determined by the relative concentrations of the metals of primary interest. In 1969, of the 501,760 tons (metric) of zinc mined domestically, 63% was in zinc ores, 19% in lead-zinc ores, 9% in lead ores, 6% in copper-lead-zinc ores, and 4% in other ores. The average zinc content of the domestic ores was 3.93%. Imported ores are generally richer in the prime metals. In 1969, 512,560 tons of zinc were imported in foreign ores, and 297,560 tons were imported as slab metal (88). Zinc/cadmium ratios in selected ores are reported in Table 8. Chizhikov (86) quotes a value of 200 for the mean of zinc/cadmium ratios in geological reserves, a value which is approximately twice the ratio of the rates of production of zinc and cadmium in the U.S. (Table 1). This difference may be explained in part by the significant U.S. imports of zinc and cadmium, as metallic slabs and concentrated ores and flue dust, in ratios different from that encountered in the primary ores. Imports of the metal and ores have changed markedly in the past years, as the U.S. producers, faced with a cost-price squeeze and high costs for pollution-control equipment, have closed several domestic smelters (five in the period 1969-1971).

Little information is available on the contamination of the environment in the mining of the polymetallic ores containing

Table 8. Zinc/cadmium ratios in selected ores.^a

Ore	Zn/Cd ratio
Zinc ore, Upper Silesia	435
Zinc ore, Belgian factories	415
Zinc ore, Broken-Hill, Australia	250
Zinc ore, Joplin deposit, USA	161
Copper-zinc deposits	333
Lead-zinc deposits	250

^a Data of Chizhikov (86).

cadmium. The major potential sources of contamination are from the particulate emission during mining and the leaching of cadmium from the overburden. The zinc content is, however, low, ranging from less than 2% in the overburden to 3.9% in the ore, so that the amount of cadmium lost via these mechanisms is expected to be low. Acid waters will, however, dissolve the sulfide ores and have been reported to accumulate as much as 42 ppm Cd, compared to more common values for mine waters of 0.1–2 ppm.

The ores are enriched primarily by flotation to yield concentrates containing 40–60% prime metal. Since the initial concentration of prime metal is of the order of several percent, most of the original mass of the ore will be discarded in the tailings. The cadmium in the ores will generally concentrate with the zinc but there may be a slight fractionation between the cadmium and zinc between concentrate and tailings. Illustrations of the recovery of cadmium in the concentration of lead-zinc ores are presented in Table 9. These values and similar studies by Vinogradov (44) suggest that 18–36% of the cadmium in polymetallic ores is

Table 9. Distribution of cadmium in ore concentrates and tailings.^a

Ore	Cadmium concentration %	Cadmium content, % of cadmium in ore	Ratio Zn/Cd
Ores from the			
Caucasus	0.04	100	240–280
Zinc concentrate	0.17–0.20	57	240–280
Lead concentrate	0.04–0.06	10	220–250
Tailings	0.004–0.009	33 ^b	220–380
Ores from Altai	0.020–0.028	100	330–660
Zinc concentrate	0.06–0.01	78	480–910
Lead concentrate	0.011–0.017	4	400–530
Tailings	0.005–0.007	18	160–230

^a Data of Chizhikov (86).^b This value is not consistent with the values reported for the cadmium concentration in the ores and the tailings.

retained in the tailings but that the fraction of zinc retained in the tailings is lower. By comparison, it is estimated in the ORNL study on cadmium (87) that 8% of the zinc and 11% of the cadmium in the original ore are retained by the tailings (Table 10).

The cadmium concentration in tailings is low, and losses from the tailings to the atmosphere should not be significant. Davis and his associates (2) estimate that wind loss from tailings amount to 0.2 lb/ton of cadmium mined, a figure that is unsubstantiated. However, the conclusion reached by Davis et al. (2) that wind losses contribute a negligible fraction of the cadmium emissions is undoubtedly valid. Leaching by acid waters is of greater concern than wind losses, but no statistics are available on the rate of dissolution of cadmium from tailings.

Table 10. Zinc recovery and Zn/Cd ratios during ore concentration.^a

Ore	Ore mined $\times 10^{-4}$, tons	Zn content of ore $\times 10^{-4}$, tons	Tailings $\times 10^{-4}$, tons	Zn in tailings, %
Zinc	9.09	0.411	8.451	0.24
Lead-Zinc	1.95	0.117	1.607	0.37
Lead	6.54	~0.040	6.214	~0.27
Other	2.29	0.034	2.195	0.11
Avg.	19.87	0.602	18.467	0.25
Zn/Cd		200		160

^a Data of Fulkerson and Goeller (87).

Table 11. Composition of ore concentrate and representative samples of flue dusts from roasting and sintering operations.*

Sample	Zn/Cd	Cd, %	Zn, %	Pb, %	Fe, %	Cu, %	S, %
Ore concentrate	256	0.18-0.20	45.9-52.6	1.8-2.9	6.7-10.8	0.6-1.6	25.6-32.2
Flue dust from roasting furnace	246	0.1-0.18	30.5-38.9	2.5-5.0	4.8-6.3	0.7-1.0	15-19
Dust from electrostatic precipitators from roasting furnace	48	0.5-0.66	22-33	20-34	3.1	0.35	~16
Flue dust from sintering machine	98	0.55	54	2.1	—	1.2	3.0
Dust from sintering machine collected in cyclone	136	0.27-0.55	53.4-58.1	1.6-3.1	—	1.1	4.3-5.5
Dust in exhaust from cyclone	5	3.5-8.8	22-44	95-37.1	—	0.22	7.1
Agglomerate	356	0.16	60.1	1.6	9.6	1.28	1.37

* Data of Chizhikov(86).

Metallurgical Processing

Major losses of cadmium occur during the processing or concentrations of zinc ores, lead ores, and, to a minor extent, copper ores. The extent of emission will depend on the metallurgical process employed and the age and condition of the processing plant, and whether cadmium is recovered at a particular installation. Of the 14 plants that produced primary zinc in the U.S. in 1969, only eight produced cadmium metal. There is no information on the fate of the cadmium content of the ores processed in the remaining six plants.

The principal source of cadmium is the zinc ores. These are first roasted to oxidize the sulfide and then treated by either pyrometallurgical or electrolytic processes.

Pyrometallurgical Recovery of Zinc

Roasting is carried out at temperatures of 700-1200°C. The amount of cadmium vaporized during roasting increases with temperature and ranges from 10 to 25%. The dust from the roasting operations is collected in electrostatic precipitators or bag filters, and the SO₂ either dispersed from a high stack or piped to a sulfuric acid plant. Comparison of the representative analysis of dust from an electrostatic precipitator with that in the ore concentrate to a roasting plant (Table 11) shows a considerable enrichment of both cadmium and lead in the dusts. The sulfur in the dusts is mainly in the form of sulfates (Table 12).

The roasted ore is sintered to drive off

residual sulfur and to agglomerate the ore. The dust from the sintering operation is led to collectors and then vented to the atmosphere. Typically 15-20% of the initial cadmium accumulates in the dust obtained during sintering (86). Examination of Table 11 shows that the cadmium/zinc ratio in the dust from the collector is somewhat higher than in the ore concentrate and that the fine dust passing through the cyclone is considerably enriched in cadmium and lead. The plant for which data are presented in Table 11 employs a relatively inefficient cyclone collector to remove the dust from the flue gases leaving the sinter plant; more efficient electrostatic precipitators and bag filters are more representative of industry practice. It should be noted that the sulfur content of the dust escaping the cyclone collector is less than half the value of that in the dust (mainly sulfates) from the roasting plant. The water-soluble fraction of the cadmium in the dust is expected to be cor-

Table 12. Composition of zinc and cadmium compounds in the dust from an electrostatic precipitator of a roasting plant as determined by solvent extraction.*

Solvent	% Extracted		Compounds extracted
	Cd	Zn	
Water	69.0	67.0	Sulfates
3% H ₂ SO ₄	8.6	7.3	Free oxides
10% H ₂ SO ₄	14.5	14.0	Ferrites (CdO·Fe ₂ O ₃ , ZnO·Fe ₂ O ₃)
Residue	6.7	13.9	Sulfides

* Data of Chizhikov(86).

respondingly lower. The amount of cadmium recovered in the flue dust from the sintering machine may be increased by adding chlorides to the charge fed the sintering machines. In this case, the degree of cadmium removal reaches 70–80%.

The agglomerate from the sinter plants will typically retain more than 50% of the cadmium content of the ore. The agglomerate containing the zinc and cadmium oxides is reduced with carbon and carbon monoxide. The resulting metals are distilled either batchwise (in plants utilizing horizontal or Belgian retorts) or continuously (in plants utilizing vertical retorts or blast furnaces). In the batch process most of the cadmium is carried over during the initial stages of the distillation (Table 13). In the continuous process the cadmium is distributed between the blue powder (approximately 5% of the distillate) and the condenser dust in the concentrations shown in Table 14. The condenser dust is redistilled.

According to Chizhikov (86), approximately half of the cadmium present in the sinter passes into the zinc metal to yield an average cadmium concentration of 0.12%, and the concentration of cadmium in the residual slag is approximately 0.05%. The residual slag is retreated when high recoveries of cadmium are sought.

Hydrometallurgical Recovery of Zinc

In the hydrometallurgical process, the ore concentrates are roasted in a single multiple-hearth unit, in which approximately 20% of the cadmium is volatilized (86). The zinc concentrate is leached with dilute sulfuric acid. Most of the cadmium passes into solution as the sulfate; 9–22% remains in the residue. The cadmium in the sulfate solution is deposited together with copper and lead by addition of zinc dust 62–86% of the cadmium being precipitated (86). The zinc is electrodeposited on aluminum cathodes from the purified sulfate solution. In 1969, electrolytic recovery accounted for approximately 41% of the primary zinc production (89).

Cadmium Distribution in Lead and Copper Production

Lead and copper concentrates recovered from polymetallic ores or from residues from zinc production contain varying quantities of zinc and cadmium. The extent of recovery of cadmium from the processing of these ores and residues depends on the initial cadmium concentration. This will be illustrated for a few case studies selected by Chizhikov (86).

In a lead production plant, 70–80% recovery is claimed for the cadmium in the

Table 13. Composition of distillate from batch unit.*

Time period, hr	Cd, %	Zn, %	Pb, %	As, %	Fe, %	Cu, %	% of Zn distilled	Zn/Cd
0–6	0.16	99.0	0.75	0.0007	0.05	0.006	60	620
6–12	0.04	98.7	1.56	0.0005	0.07	0.007	30	2470
12–18	0.03	97.8	2.10	0.003	0.10	0.008	10	3260

* Data of Chizhikov (86).

Table 14. Concentrations of cadmium and other trace metals in the products from zinc distillation.*

Condensate	Cd, %	Zn, %	Pb, %	Cu, %	Fe, %	% of total condensate	Zn/Cd
Condenser dust	0.13	91 ^b	0.8	0.2	3.2	~95	700
Zinc blue powder	0.7–1.1	84–90	1.0–1.5	—	0.3–0.9	~5	~97

^b This value, listed as 61 in the original literature (86), is believed to be a typographical error and has been changed to 91.

* Data of Chizhikov (86).

dust from the sintering and smelting operations. The concentration of the cadmium in the dust from the sintering operation was 0.35–0.36%, and the water-soluble fraction of the dust ranged from 6 to 25%. The average particle size of the sinter dust collected in an electrostatic precipitator varied from 0.4 to 1.2 μ . The dust from the smelters had cadmium concentrations that varied from 1.6 to 6.5% and water-soluble fractions that ranged from 0 to 11%; the dust was submicron in size. Information, admittedly of a qualitative nature, supplied by smelter operators to Davis et al. (2) suggested that emissions were in the 4–8 μ size range. It is not possible to judge whether these data are spurious or indicative of growth of the emitted particles by condensation and agglomeration in the stack.

Cadmium vaporizes to a much smaller extent in copper plants, and a significant fraction of the cadmium in the ore concentrate passes into the slag from the smelter. Balances on smelters of different design are presented in Table 15 and on a Bessemer converter in Table 16. From Tables 15 and 16 it can be estimated that roughly one third of the cadmium losses passes into the slag, and the remaining two thirds are lost to the atmosphere.

Table 15. Distribution of cadmium in product streams from copper smelters of different design.*

Stream	Cadmium recovery, %	
	Reverbatory smelting	Blast furnace smelting
Converter matte	49.1–56.3	38.4
Dust collected	6.8–9.2	22.9
Waste slag	7.1–12.6	16.6
Gas losses	29.1–29.8	22.1

* Data of Chizhikov (86).

Table 16. Distribution of cadmium in Bessemer processing of matte from reverbatory and blast furnace smelting.*

Stream	Cadmium recovery, %
Crude copper	—
Converter slag	35.3
Flue dust	6.2
Gas losses	58.5

* Data of Chizhikov (86).

Production of Cadmium Metal

Cadmium is recovered from the blue powder collected during the distillation of zinc, the cadmium fraction from zinc distillation units, the copper–cadmium filter cakes deposited from sulfate solutions, and the dusts from roasters, sintering machines, and fuming furnaces used in zinc, lead and copper production.

Prior to 1910, cadmium was produced by distillation in retorts similar to those used for zinc recovery. Cadmium losses from the distillation process were high, often 40–50% of the initial quantity (86).

At present, most of the cadmium is recovered by hydrometallurgical processes. The cadmium is dissolved in sulfuric acid, and cadmium sponge is deposited by addition of zinc. The process may be repeated several times to increase the purity of the cadmium. Finally the sponge is redissolved, and the cadmium is deposited electrolytically. Recoveries of cadmium in the hydrometallurgical process are reported to exceed 90% (86, 89).

Summary on Emissions from Smelters

The amount and physical and chemical state of the cadmium emitted by smelters will depend on plant design and on the efficiency of the particulate collection devices on the individual units within a plant. The emission from sinter units and retort stills will consist mainly of the oxide (or the chloride when chlorides are added to the charge to the sinter unit), whereas sulfates may constitute a significant portion of the emissions from roasters. The particles will vary in size from the submicron range to about 8 μ and have a Zn/Cd ratio varying from the extremes encountered in the cadmium and zinc purification stills. On the average, because of the higher volatility of cadmium, the Zn/Cd ratio in the atmospheric losses from smelters will be lower than those in the ores processed. Values for smelter recovery efficiencies of 75% for cadmium and 89–97.5% for zinc are quoted by Heindl (90), suggesting that, for an ore with a Zn/Cd ratio of 200, the Zn/Cd ratio

in the portions not recovered (losses to the atmosphere and in the slag) will range from 20 to 88.

Transport of Emissions from Smelters

The fraction of the stack emissions in the vicinity of the smelter will depend upon particle size, varying from a negligibly small value for submicron particles to practically complete deposition for particles greater than 10 μ . Uncertainty regarding the particle size distribution at the source and the dynamics of particle growth in the atmosphere preclude any attempt at quantitative modelling of the particle deposition rates. Of the cadmium deposited, the sulfates and chlorides may be leached from the soil by rainfall, but the oxides, which have a negligible vapor pressure, will accumulate in the soil, other than the small amounts taken up by vegetation or windblown from the surface. It is, therefore, expected that the soils surrounding smelters may have high concentrations of cadmium and zinc corresponding roughly to the cumulative deposits of emissions from the local smelter, less the small amounts taken up by the vegetation and leached by precipitation. Some selected studies of soil concentrations and dustfall surrounding smelters support this conclusion, at least to an order of magnitude approximation.

East Helena, Montana: An extensive study (41) of the pollution surrounding lead and zinc smelters in East Helena, Montana, revealed concentrations of zinc up to 5200 ppm and cadmium up to 160 ppm in the soils in the vicinity of the smelter. From measurements at different radii from the smelter and at depths up to 25 cm it was estimated (41) that 5100 tons of zinc and 260 tons of cadmium had been added to the soils within a radius of 1.0–16 km from the smelter stack. The Zn/Cd ratio of about 20 is, as anticipated, considerably smaller than the ratio in geological reserves. The zinc production at the East Helena plant was about 80 tons/day at the time of the survey, and the plant was reported to have a zinc recovery of 91%. If the zinc in the

slag is assumed to be a third of the total losses, a rate of zinc atmospheric emission of about 5 tons/day is estimated.

The solubility of the dust emitted by the different units in the smelter ranges from near zero to 70% from the roasters, with a mean of probably less than 15%. The diffusion of the insoluble fraction into the soil is low, and most of the dustfall is retained in the surface layers. The amount of zinc accumulated in the soil, therefore, corresponds to the cumulative emission of about 1000 days at full production.

These calculations support the conclusion that a major fraction of the emission from smelters accumulates in the surrounding soil. The estimates of emission and acculation given above are too approximate to permit a closure of a material balance and to determine by difference the amount of cadmium transported to distant locations either directly by long-range aerial transport or indirectly by plant uptake, leaching, and transport in surface waters.

The distribution of cadmium and the Zn/Cd ratio in the top 25 cm of the soil is shown in Table 17, taken from the smoothed data of the East Helena study. It can be seen that the Zn/Cd ratio increases with depth but is lower than that in geological reserves, even at the 15–25 cm depth. Soils collected outside the Helena valley as part of the study had a mean cadmium concentration of 0.8 ppm and zinc concentration of 58 ppm (Zn/Cd = 74). Low Zn/Cd ratios were also observed in the settleable dust and suspended particulate providing support for the postulate that the relatively low Zn/Cd ratio in the soil reflected the low Zn/Cd ratio at the source and not a selective leaching of zinc from the soil.

Table 17. Cadmium content and Zn/Cd ratios in uncultivated soil surrounding East Helena Stack.*

Depth of soil, cm	1.8 km from stack		3.6 km from stack		7.2 km from stack	
	Cd, ppm	Zn/Cd	Cd, ppm	Zn/Cd	Cd, ppm	Zn/Cd
0–2.5	68	16	17	14	4	12
5–10	30	33	7	25	2	15
15–25	3	70	2	42	1	33

* Data of Miesch and Huffman (41).

The uptake by vegetation may be estimated from the concentration of cadmium in the crops. The concentration of cadmium in plants sampled from ranches within 6 km of East Helena reported in the EPA study (41) include 0.3–3.2 ppm (wet-weight basis) for alfalfa, 6.3 ppm for barley straw, 0.1–1.2 ppm barley kernel, and 1.2–9.8 ppm pasture grass. As a rough gauge of cadmium removal from the soil by crops, the above value will be assumed to be an average value for the region, and a crop yield of 2 tons/acre for alfalfa selected. Based on an assumed average concentration of 2 ppm in alfalfa, the cadmium removal per crop in an area with a 6-km radius is 1.2 tons/yr. The plant uptake per crop is less than a percent of the cadmium accumulation in the soil and does not provide a significant mechanism for cadmium removal from the soil, although locally it may be a major route for human and animal cadmium intake.

Annaka City Smelter, Japan: Distributions of cadmium and zinc in the soil 900 m from the smelter chimney (42) are shown in Table 18. The ratio Zn/Cd in the surface layers is again lower than in geological reserves, suggesting a preferential emission of cadmium from the smelter stack. As was the case for East Helena, the depth of penetration of zinc and cadmium in the soil is seen to be small.

Metal Processing Furnaces

The major source of atmospheric emissions of cadmium other than smelters was identified by Davis et al. (2) as metal treatment furnaces. Fulkerson and Goeller (87)

Table 18. Cadmium content and Zn/Cd ratio in soil 900 m from Annaka City stack.*

Depth, cm	Cd, ppm	Zn/Cd
0-2	81	54
5	44	36
10	32	41
20	6.9	78
30	1.4	100
40	0.4	200
60	0.3	207

* Data of Kobayashi (42).

have more recently reevaluated the cadmium emission from the treatment of scrap steel. Based on figures of 2830 tons of cadmium for electroplating, 416,000 tons of zinc with an average cadmium content of 0.023% for zinc galvanizing, 76 million tons of finished steel, and 26 million tons of steel scrap, they estimate that 1000 tons of cadmium were volatilized during the remelting of steel scrap in 1968. The amount emitted will depend on the pollution abatement devices. For an assumed 90% efficiency in the dust collectors they obtain an emission estimate of 100 tons, approximately one tenth of the value estimated by Davis et al. (2). The amount of cadmium emitted may, however, be much higher if the collected dust is recycled to the furnaces. The dusts from steel remelting furnaces have iron oxide contents which range from 25% to over 90%. Ores with a high concentration of iron oxide may be recycled, thus providing an opportunity for enhancing the emission of the volatile cadmium compounds. The fraction of the collected dust that is recycled is not known, so that the emission of cadmium from furnaces treating plated steels cannot be estimated with any accuracy. It will here be assumed, somewhat arbitrarily, that as a consequence of inadequate air pollution control from older units and some recycle that 500 tons of cadmium were emitted and 500 tons deposited in dumps in 1968.

It should be noted that, in addition, zinc products contain small amounts of cadmium and that the disposal of zinc products also contributes to cadmium emission. Table 19 gives the maximum permissible cadmium concentrations in the different grades of zinc marketed. If the different grades of zinc

Table 19. Cadmium content of different grades of zinc and amounts marketed in 1968.

Grade	Maximum cadmium, %	Zinc production, metric tons
Special high	0.003	418,000
High	0.03	106,500
Intermediate	0.40	51,500
Brass special	0.50	68,900
Prime western	0.50	366,000

contained the maximum permissible cadmium concentration, they would contain an amount of cadmium equivalent to 36% of the total U.S. consumption. The cadmium content is, however, lower than the maximum limit for the different grades and corresponds to approximately 7% of production (87).

The zinc content of particles discharged from different metal treatment furnaces is relatively high, even for ferrous metal furnaces (Table 20). The particle sizes of the zinc fumes from these furnace types is reported (91) to be in the range 0.03–0.3 μ . Although cadmium emissions were not measured, they are expected to show a similar pattern.

Coal Combustion

Estimates of the emission of cadmium from coal fired units must depend on the efficiency of collection of the cadmium in the particulate collection equipment. A study by Bolton et al. (92) of the efficiency of collection of trace elements in the fly ash of a cyclone-fired boiler equipped with electrostatic precipitators indicated that the collection efficiency was high for cadmium and most other trace elements other than mercury. The collection efficiency for cadmium can therefore be approximated by that for total particulate collection. If it is assumed that for the 455 million tons of coal consumed in 1968, the average particulate collection efficiency was 80% and the average cadmium concentration was 1.0 ppm, an annual emission of 91 tons is obtained, close to the value of 100 tons estimated by Davis et al. (2) but lower than the upper bound of 1000 tons given by Fulkerson and Goeller

(87) based on the maximum concentration of cadmium in coal. Obviously, the emission of cadmium from coal-fired units is strongly dependent on the cadmium concentration in coal and on the collection efficiency for particulate. More data are needed on cadmium concentrations in coal and in the different size fractions of the ash emitted from furnace combustion chambers of representative design.

Estimations by Klein and Russell (93) of fallout surrounding a 650 MW power plant in service since 1962 showed a cumulative cadmium emission of 18 tons for a cumulative coal consumption of 10⁷ tons. Prorating these values to a coal consumption in the United States of 455 million tons/yr would yield a rate of cadmium emission of 820 tons/yr. It should be noted, however, that the Zn/Cd ratio in the estimated fallout was only 9, suggesting that the estimated cadmium emission may be more than an order of magnitude too large.

Cement Production

Goldberg (E. D. Goldberg, Univ. Calif., San Diego, personal communication) estimated the world wide emission of cadmium from cement manufacture was 100 tons in 1962 assuming that the concentration of cadmium was 0.3 ppm in shale and 0.035 ppm in carbonates, and that all the cadmium was volatilized. It is here estimated that the U.S. emission in 1968 was 3 tons, assuming that 80% of the emissions were captured in particulate collection devices.

Incineration

Davis (2) estimated that 86 tons of cadmium were incinerated in 1968, based on a disposal of 40% of the annual average consumption of cadmium for paints, pigments, and miscellaneous uses and incineration of 15% of the total wastes. A rough check of this estimate may be made using measurements by Levins (Arthur D. Little, unpublished data, 1972) of trace metals in the particulate from a municipal incinerator. Four samples were found to contain 250, 400, 200, and 1700 ppm (average 640 ppm) cad-

Table 20. Concentration of zinc in dust and fume discharged from different furnace types.*

Furnace type	Zinc concentration, %
Open-hearth steel	10–15
Electric-arc steel	26
Brass-furnace	42
Zinc-galvanizing	15
Gray iron cupola	6–7

*U.S. Public Health Service data (91).

mium and to have Zn/Cd ratios of 100, 90, 410, and 40 (average 160). For a national municipal waste generation in 1968 of 160 million tons, 15% burned in incinerators and dumps, a particulate emission of 0.007 tons/ton, corresponding to municipal unit with wet baffles (94); the total cadmium emission is 107 tons, in fair agreement with the Davis estimate. With the closing of open-burning dumps and stricter air-pollution regulations on incinerators this source of emission should be reduced significantly.

Ambient Concentration in Urban Areas

The total emission of cadmium to the urban atmosphere has been estimated as 706 metric tons/yr, with major contributions from metal processing (500 tons/yr), coal and oil combustion (120 tons/yr), and incineration of plastics and pigments (86 tons/yr). Since roughly three quarters of total suspended particulate in urban areas are of nonagricultural origin and the emission of particulate within cities is of the order of 2×10^7 tons/yr (95) the emission should yield a mean cadmium level of the order of 25 ppm. In urban air with particulate concentrations typically in the range 80–120 $\mu\text{g}/\text{m}^3$, the concentration of cadmium should have an average for all urban areas of approximately 0.002 $\mu\text{g}/\text{m}^3$, with departures from the mean determined primarily by the concentration of metal processing industries in a given city. Table 21 provides values of cadmium and Zn/Cd ratios in selected cities. The concentrations are in fair agreement with the rough number gauged from emission estimates. The Zn/Cd ratio is frequently below that in the geological reserves, possibly due to the selective vaporization of cadmium in the processing furnaces.

Measurements of dustfall in Cincinnati by Creason et al. (23) show a Zn/Cd ratio of 150 and an average cadmium concentration in the dustfall of 13 ppm, about twice the above estimate for a national average. The cadmium concentration in air in Cincinnati varied from 0.008 $\mu\text{g}/\text{m}^3$ in an urban area to 0.0035 $\mu\text{g}/\text{m}^3$ in an industrial area. The values

Table 21. Cadmium concentrations and Zn/Cd ratios in urban air.^a

City	Cd concn. arith. mean, $\mu\text{g}/\text{m}^3$	Zn/Cd
Burbank, Calif.	0.004	250
Long Beach, Calif.	0.002	75
Los Angeles, Calif.	0.009	78
Pasadena, Calif.	0.008	22
San Jose, Calif.	—	^b
Kansas City, Kansas	0.002	140
St. Paul, Minnesota	0.001	30
Kansas City, Co.	—	^c
Elizabeth, N. J.	0.005	72
Glassboro, N. J.	0.004	63
Jersey City, N. J.	0.007	32
Glen Cove, N. Y.	0.004	8
New Rochelle, N. Y.	0.017	24
New Troy, N. Y.	0.002	45
Asheville, N. C.	0.001	20
Medford, Oregon	0.001	60
Ft. Worth, Texas	0.005	20
Houston, Texas	—	^b
Salt Lake City, Utah	0.001	10

^a EPA data (96).

^b Zn = 0.12 $\mu\text{g}/\text{m}^3$.

^c Zn = 0.06 $\mu\text{g}/\text{m}^3$.

are higher than the average value derived earlier, possibly due to a concentration of metallurgical industry in Cincinnati.

The rate of deposition of cadmium from the atmosphere will depend upon the particle size, which is a function of size distribution at the source and agglomeration and sedimentation in the atmosphere. Measurements by Lee et al. (97, 98) of the cadmium and zinc concentrations in sized fractions of the suspended particulate in St. Louis are summarized in Table 22. The mass mean diameter of the particles containing zinc and cadmium are slightly larger than the mean diameter of the total suspended particulate, but the difference is not sufficiently large to effect any appreciable fractionation of cadmium between dust fall and suspended particulate. Cadmium and zinc will have half-lives comparable to that of total suspended particulate—of the order of a few days—and they will, therefore, deposit mainly in the vicinity of the source. Small particles may be transported considerable distances before deposition, and long-range transport will also occur at a slow

Table 22. Cadmium and zinc in different size fractions of suspended particulate in St. Louis.^a

	Total Particulate	Zinc	Cadmium ^b
Av. concn, $\mu\text{g}/\text{m}^3$	73	0.01	0.3
Av. mean diameter, μ	0.8	1.54	1.19
Mass, % <1 μ	54	28	42
Mass, % <2 μ	68	65	74

^a Data of Lee et al. (97, 98).

^b Second quarter. Values for Zn and total particulate are year averages.

rate by the periodic suspension of deposits by wind action and redeposition. [The ambient concentrations of particulate in rural areas has been increasing slowly in a period when the concentrations in urban areas have been decreasing (99).]

Water Transport

Quantitative data on cadmium inputs to surface and coastal waters are fragmentary. It is expected that the major inputs will be from the leaching of mine tailings, particularly by acid waters, from the emission into the atmosphere of soluble sulfates and chlorides, from the disposal of waste streams by hydrometallurgical and cadmium-plating installations, from surface runoffs in urban areas, and from the disposal of sewage sludge and effluent into water streams.

Mine Drainage: Streams and sediment in the Conway Catchment in Wales show anomalous concentrations of zinc and cadmium in both water and sediment as a consequence of drainage from old mines and periodic sediment transport by heavy rains (100). The maximum zinc concentration in the sediment exceeded one percent in the area of the mines and had a mean value of approximately 900 ppm in the estuary. Concentrations of soluble zinc compounds, probably in an ionic or weakly complexed form, were as high as 3000 ppb in the tributary streams draining the mines and 100 ppb in the estuary, compared with values of 25 ppb in streams draining unmineralized areas (Table 23). The decrease in concentration from the tributary to estuary is prob-

ably a consequence of dilution rather than self-cleansing of the stream by ion exchange with the bottom sediment (this postulate is speculative and should be tested out by field studies). Although cadmium flows were not measured, they are expected to be 0.5–1% those of zinc. No quantitative estimates are available of the amounts of cadmium and zinc leached from mines, but these are expected to be a major source of water pollution and may be inferred from concentrations in surface flows in mineralized areas.

As an example of the enhancement of pollution from mined areas, the drainage from strip mines has been found to yield an average of 30,000 tons of sediment per square mile annually, which is 10 to 60 times the yield from agricultural lands (101). Such a large enhancement of sediment drainage is not expected for zinc mines, since these are mostly subsurface, but the potential for significant drainage from mines, particularly those that are abandoned, should be noted.

Smelter Losses: Soluble salts emitted by smelters include the sulfates from the roasters, and the chlorides from sinter units. From consideration of the process details, it appears unlikely that the sum of the emissions of the soluble salts could exceed 15% of the estimated 955 tons of cadmium emitted to the atmosphere by smelters. Additional losses are expected in waste waters from the hydrometallurgical plants, but these will not exceed 10% of production, i.e., 240 tons/yr, based on consideration of the reported cadmium recovery efficiencies.

Table 23. Cadmium concentration and Zn/Cd ratio at Conway, Wales.^a

	Cd, ppb	Zn/Cd
Tributary drainage		
Mineralized area	2.5	340
Unmineralized area	0.43	55
River Conway		
Above tidal influence	0.50	67
Below tidal influence	0.67	170
Local sea water	0.76	12

^a Data of Elderfield et al. (100).

Plating Operations: Electroplating operations are highly efficient, and losses of cadmium from these should be low. For purposes of demonstrating magnitudes, a 5% loss of metal in waste plating solutions would correspond to 136 tons/yr. Cadmium concentrations in the waste stream from plating plants in the Chicago area were found to be less than 1 ppm for 72% of the samples collected, 1–10 ppm for 20% of the samples, 10–50 ppm for 6% of the samples, and greater than 59 ppm for 1.5% of the samples (79).

Sewage: From consideration of the flow of cadmium in sewage treatment plants, it appears that practically all the cadmium in the entering stream will be discharged in the effluent for installations employing only primary treatment, whereas most of the cadmium will be retained in the sewage sludge for those plants utilizing secondary treatment. Over the time interval considered, approximately half of the sewage underwent secondary treatment, so that 50% of the cadmium content of sewage would have been discharged into surface waters. The cadmium-containing sludge is disposed of by a combination of burial, addition to soil as fertilizer, incineration, or wet oxidation. The major route of cadmium into sewage is from industries processing cadmium products and from surface runoff in cities where the storm drains and sewers are combined. The estimates of industrial losses are of the order of 150 tons/yr, and the maximum value for surface runoff is 1000 tons/yr. These estimates may be compared with selected measurements of cadmium in sewage sludge and sewer effluent.

The mean concentration of cadmium in the sewage sludge of 22 communities in Massachusetts was found to be 12 ppm, with 10% of the samples having concentrations in excess of 45 ppm (102). The Zn/Cd ratio in 54 samples from the 22 stations ranged from 50 to 150. In digested sewage sludges in the Chicago area, the concentration of cadmium and the Zn/Cd ratio were found to be 70 ppm and 48, respectively, at the Calumet treatment plant and 470 ppm and 14

ppm, respectively, at the Stickney plant (79). If it were assumed, somewhat arbitrarily, that 10% of all sewage sludge had a concentration of 470 ppm, 30% had a concentration of 70 ppm, and the remainder 12 ppm, the total cadmium flux in the sewage sludge would be of the order of 650 tons/year. Since it had been earlier estimated that half of the total cadmium in sewage would be retained by the sludge, this corresponds to a flux of 1300 tons/year of cadmium. These calculations are intended only to indicate the order of magnitude of the cadmium content of sewage; reliable estimates of the cadmium content must be based on a more representative sampling of sewage sludges.

The concentration of cadmium in the effluent streams of some treatment plants are also available. At the Stickney plant referred to above, the cadmium concentration in the effluent of the preliminary treatment tank was 90 ppb, most of the cadmium was retained in sewage sludge obtained from a subsequent digestion unit, and the concentration in the final effluent was only 3 ppb (79). Concentrations of cadmium in the primary sewage effluent of the City and County of Los Angeles of 20 and 80 ppb have been measured (103). Based on a per capita waste water flux of 120 gal/day, the concentrations of 20 and 80 ppb extrapolate to national cadmium flows in sewer effluents of 600 and 2640 tons/yr, respectively. Although more measurements of cadmium concentration are needed before reliable estimates of cadmium flow in sewage may be obtained, the value is expected to be of the order of 1150 tons/yr.

Further evidence of the importance of sewage as a major route for cadmium input into the environment is the enrichment of the cadmium in the coastal sediments in area of 25–130 km² in the vicinity of Southern California coastal sewage outfalls by factors of 20 to 100 relative to sediments far from the outfall areas (104, 105).

River Transport: The cadmium concentration and fluxes in the Mississippi-Missouri and other selected rivers based on the

measurements of Durum et al. (63) are shown in Table 24. Even after allowance is made for the problems of nonrepresentative sampling, the rate of cadmium flow and Zn/Cd ratios appear to be anomalous. The peak cadmium flow of 5690 tons/yr in the Mississippi-Missouri Rivers corresponds approximately to the total U.S. cadmium consumption (6020 tons/yr) and would appear to exclude losses from industrial operation as the major source of contamination. The cadmium flow increases rapidly in the mineralized area about the tristate Tennessee-Missouri-Kentucky border, suggesting that the increase in the cadmium flux results

from weathering or mine drainage. But if this were the case, the Zn/Cd ratio should be close to that found in geological reserves. The anomaly remains unexplained, and may be a consequence of analytical difficulties (e.g., by selective removal of zinc or contamination by cadmium in the 0.45 μ filters through which the samples were passed). In contrast to the above observation of anomalously low Zn/Cd ratios, analyses of sediments in Massachusetts streams (Table 25) show considerable contamination by cadmium and zinc without significant departure of the Zn/Cd ratio from the range found in geological reserves (102).

Table 24. Cadmium concentrations and flows in selected rivers.*

Location	Flow, ft ³ /sec	Cd, μg/L	Cd flow, ton/yr	Zn/Cd	Date	Comment
Mississippi-Missouri River (in order of increasing distance from source)						
North Dakota 7	28,000	1	25	20	10/9/70	
Nebraska 1	47,400	2	84	10	10/9/70	
Nebraska 2	47,400	4	168	5	10/9/70	
Missouri 2	53,500	14	665	—	10/14/70	
Missouri 3	54,000	8	386	0.6	10/14/70	
Missouri 5	60,000	25	1,340	1.6	10/5/70	
Missouri 7	155,000	8	1,100	—	10/13/70	
Illinois 18	298,000	16	4,350	—	10/13/70	
Illinois 19	312,000	12	3,340	—	10/14/70	
Missouri 9	319,000	20	5,690	1.5	10/15/70	
Tennessee 12	288,000	8	2,060	16	10/14/70	
Louisiana 10	328,000	6	1,750	—	10/20/70	
Louisiana 11	328,000	6	1,750	—	10/20/70	
Tributaries to Mississippi-Missouri						
Kentucky 5 (Ohio R.)	50,000	20	892	9.5	10/23/70	Junction between Missouri 9 and Tennessee 12
Alabama 16 (Tenn. R.)	38,100	90	3,080	—	10/21/70	
Illinois 11 (Ill. R.)	22,100	1	20	30	10/6/70	Junction between Missouri 7 and Illinois 18
Selected rivers with Cd concentrations exceeding minimum detectable limit (1 μg/L)						
Washington 14 (Columbia R.)	110,000	2	196	5	10/6/70	
Pennsylvania 19 (Susquehanna R.)	11,450	5	51	4	10/14/70	
Pennsylvania 36 (Alleghenny R.)	23,500	1	21	60	10/12/70	
California 15 (Sacramento R.)	15,400 (est.)	2	27	—	10/7/70	
Arizona 7 (Mineral Creek)	10 (est.)	30	1	320	10/8/70	

* Data of Durum et al. (63). Locations as defined by Durum et al.

Table 25. Cadmium and zinc in sediments in Massachusetts. *

Location	No. of samples	Cd,	Zn,
Blackstone	13	150.0	4000
		35.7	953
		2.8	88
North River	12	5.5	985
		1.4	343
		0.0	9.0
South River	3	0.3	17
		0.3	15
		0.0	11
Boston Harbor	18	7.5	350
		1.85	131
		0.00	11
Quinsigamond River	6	0.6	92
		0.36	52
		0.3	28
Lake Quinsigamond (grab)	4	5.5	730
		3.05	420
		0.9	130
Lake Quinsigamond (core)	4	2.8	380
		2.2	268
		1.7	190
Lake Quinsigamond	8	5.5	730
		2.63	344
		0.9	130
Massachusetts Bay	9	2.0	100
		0.38	33.4
		0.00	8.0

* Data of Isaac and Delaney (102).

Coastal Waters: The discharge of cadmium into coastal regions in river efflux and in sewer outfalls may amount to several thousand tons per year, based on the preliminary values reported above for surface water and sewer effluent concentrations. The cadmium is mainly in solution; Preston et al. (56) find that 18% of the cadmium and 44% of the zinc in seawater from shoreline and offshore areas of the British Isles are retained by filters of 0.2 μ pore size. From measurements of concentration of seven metals (Zn, Fe, Mn, Cu, Ni, Pb, Cd) in areas ranging from the relatively confined east Irish Sea to the open Atlantic, Preston et al. concluded that the concentrations of the metals examined were in general not significantly higher than those in the open Atlantic Ocean adjacent to the British Isles but that they were significantly higher in the shoreline waters near industrial

sources (more specifically, the east Irish Sea, where the most extensive measurements were made). Preston et al. furthermore found (56) a negligible difference between concentrations measured in 1961 and 1970 except for cadmium, the concentration of which decreased 24% in the 9-yr time interval. Their study suggests that cadmium contamination is confined to shoreline waters. The failure to detect significant offshore contamination by the metals may be a consequence of deposition of most of the heavy metals in estuaries and near-shore sediment.

It is instructive to compare man's input of cadmium to the oceans with the natural fluxes. Bertine and Goldberg (21) estimate the global value of the sedimentary flux of cadmium to be 500 tons/yr by assuming that the cadmium concentration in the solids transported to the ocean (2.73×10^9 tons/yr) due to weathering is that in igneous rocks (ca. 0.20 ppm). The fluxes from man's input into coastal waters are therefore much greater than that estimated for weather mobilization. It should be noted, however, that the present concentration of cadmium in the oceans ca. 0.11 ppb, is much lower than that which would be calculated from the cumulative natural input, suggesting that cadmium is being continuously deposited from ocean waters. From the concentration of cadmium in the oceans and the sedimentation rate it is estimated that the retention time for cadmium in the oceans is 500,000 yr (106).

Summary

The available data on ambient concentrations and emissions of cadmium in the environment are fragmentary and sometimes of questionable validity but, nevertheless, permit the determination of order of magnitude values for the major fluxes and reservoirs of cadmium in the environment. These estimates are summarized in Table 26 and Figure 5. For completeness, missing data have been estimated or guessed and the reader is directed to the earlier discussion of the various fluxes for an appreciation of the uncertainties in the figures cited.

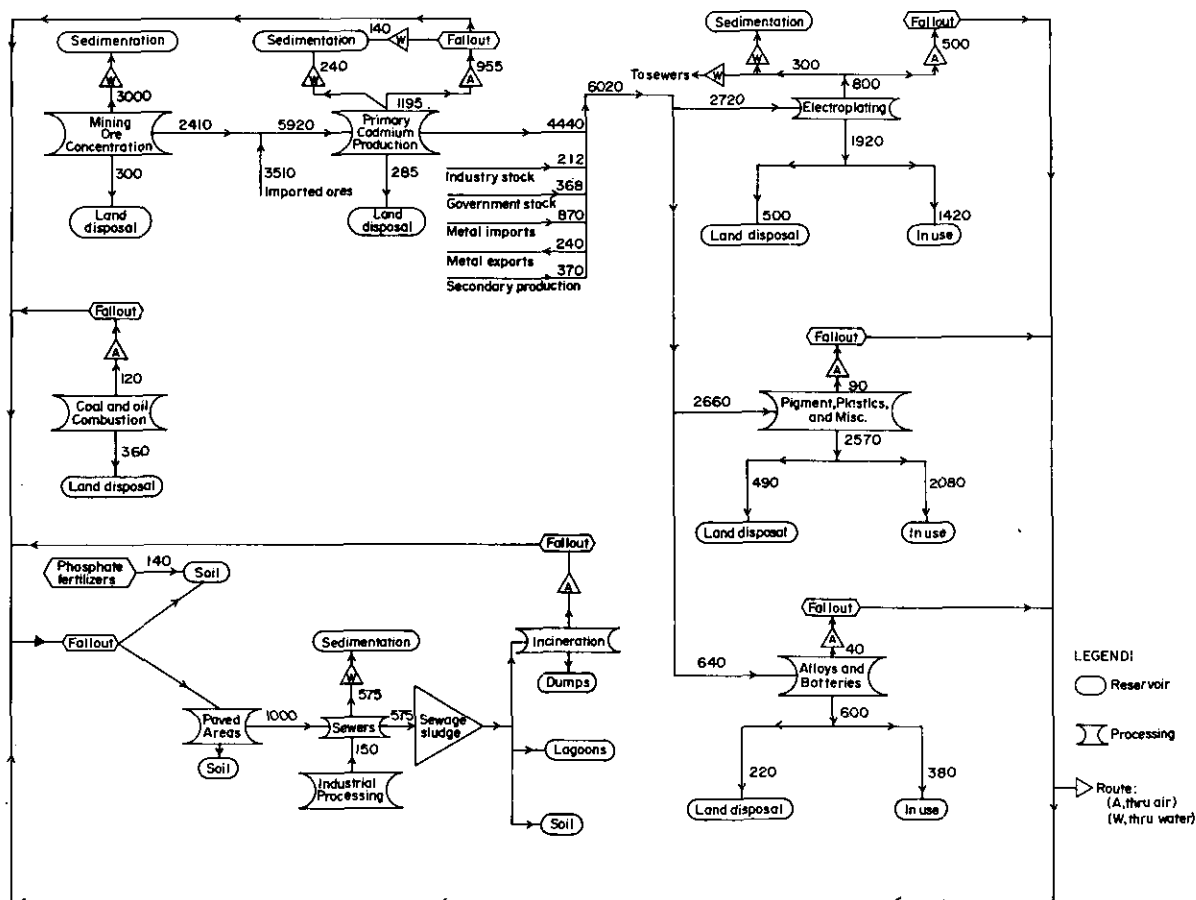


FIGURE 5. Rates, routes, and reservoirs of cadmium in the environment.

Table 26. Estimated rates of emission of cadmium during production and disposal of cadmium products for 1968.

	Mining and ore concentration, tons/yr	Primary cadmium production, tons/yr	Electroplating, pigment and plastic formulation, tons/yr	Coal and oil combustion, tons/yr	Losses during use and disposal			Total, tons/yr
					Cadmium-plated metals, tons/yr	Pigment, plastics, and miscellaneous, tons/yr	Alloys and batteries, tons/yr	
Air contamination		930		120	500	90	40	1680
Water contamination	3000	240	300					3540
Soil contamination								
Accumulation in service					1420	2080	380	4890
Land disposal (dumps, land fills, slag pits, mine tailings)	300	310		360	500	490	220	2180

Air Contamination: From consideration of the overall flow, the major sources of contamination of the atmosphere are identified to be the emission from smelters, from furnaces reprocessing cadmium containing metals, and from coal-burning equipment. In all cases, the emission of cadmium could be greatly reduced by use of efficient particulate collection equipment and, in the case of smelters, by replacement of pyrometallurgical by hydrometallurgical processing. A substantial fraction of the atmospheric emissions is deposited in the vicinity of the sources, as evidenced by the accumulation of cadmium in the soil surrounding smelters and boilers. Measured ambient concentrations of cadmium are in fair agreement with the values estimated from emissions, demonstrating the value of crude models of transport for obtaining preliminary estimates of exposure levels.

Water Contamination: The high fluxes of cadmium in the Mississippi River as it flows through the mineralized areas in Tennessee-Missouri-Kentucky, supported by similar observations in Conway, Wales, suggest that mine drainage may be the dominant source of water contamination. In addition, substantial amounts of cadmium are found in sewage, in amounts greater than would be expected for losses from cadmium-plating facilities. The fallout of atmospheric cadmium and subsequent entrainment in surface run-offs may account for the high sewage load. Most of the cadmium in surface flows is in solution. It should be noted that the cadmium solubility is strongly dependent on solution composition, particularly acidity, and that there is a potential danger that cadmium deposits that are presently immobilized may be dissolved if the acidity of rains, mine drainage, or surface run-offs increases. Cadmium in sewage is partly retained in the sludge and partly lost in the aqueous effluent (with the major fraction retained in the sludge in plants with secondary treatment). The cadmium losses to water streams appears to be ultimately deposited in the sediments in estuaries and

along the shoreline, and may create a problem in these ecologically sensitive areas.

Soil Contamination: Cadmium buildup in soils surrounding smelters or other major sources has reached unacceptably high levels. The concentration of cadmium in the top layers of the soil may be estimated from the cumulative emission from the local sources. Additional cadmium is added to soils as contaminants in phosphate fertilizer and sewage sludge used for soil conditioning. Removal of cadmium from soils by plants, although significant as a path to man, does not provide a mechanism for appreciable depletion of the accumulated cadmium deposits.

Recommendations

1. In order to facilitate the modelling of transport of cadmium through the environment, particle size distribution and chemical state should be measured in addition to mass emission at the sources of discharge into the environment.

2. The cadmium content of sewage, based on limited measurements, appears inexplicably high. Additional data are needed on the amounts and origin of cadmium in sewage.

3. The contribution of mine drainage to surface water cadmium contents needs to be quantitatively determined.

4. Material balances, albeit crude, and departures of Zn/Cd ratios from their natural values should be used, whenever possible, to test the consistency of data reported for ambient concentrations.

Effects on Man and Experimental Animals

The very extensive literature on the biologic effects of cadmium has been the subject of a number of recent reviews (13, 30, 107, 108). Much information has come from studies of acute toxicity rather than from those directed to evaluating low level environmental effects.

Metabolism of Cadmium

Although there is little doubt that man and other mammals absorb cadmium through

the lung and by mouth, there have been very few studies designed to estimate quantitatively human uptake from the environment.

Tipton and Stewart (109) described a balance study in three normal subjects over periods from 140 to 347 days. Using atomic absorption methods, the amount of cadmium and a number of other metals were determined in the diet, and the amount excreted in the urine and feces was measured.

The subjects were reported to have ingested an average of 170 μg Cd/day from the diet and to have excreted about 42 μg /day in the feces and 94 μg /day in the urine. Friberg et al. (30) point out that these results indicated an absorption of 75% of the intake, much higher than reported by others. The urinary excretion levels also seemed very high and it seems possible that analytical errors resulted from sodium chloride interference (30).

Bostrom and Webster (110) studied the intake in a human for short periods of 5 days. They found cadmium intake levels of 12 μg /day in each of two periods and fecal excretion of about 5 μg /day. The short duration of the study would make interpretation of absorption uncertain.

Rahola et al. (111) recently reported on work in progress in which five human subjects were given orally $^{115}\text{Cd}(\text{NO}_3)_2$ mixed with a kidney suspension. The dose used was 100 μg as Cd, containing about 5 μg ^{115}mCd , and body retention was studied by whole body counting. Urine and fecal excretion were also followed. About 6% of the dose appeared to have been retained at two weeks. The subsequent rate of decrease in the amount retained in the body was extremely slow. The half-time for body retention was in excess of 100 days. Therefore total absorption of the oral dose of cadmium probably was not much greater than the 6% found to be retained after 2 weeks (Figs. 6 and 7).

Various animal studies also suggest that the absorption of cadmium from the gastrointestinal tract is poor. For example, Decker et al. (112) found 2.6% of a single oral dose of ^{115}Cd in the liver and kidneys of

rats three days later. At 7 and 15 days after administration 2.0% of the dose was present in these organs. Thus, at least 2.6% of the dose had been absorbed, but probably not much more than in view of the fact that little or no radioactivity could be detected in muscle, lung, bone, spleen, and urine.

As part of a chronic toxicity study in rats, Decker et al. (113) measured cadmium levels in the kidney and liver. These contained about 0.3–0.5% of the dose of Cd ingested in one year. Since 50–75% of the body burden will be in these organs, it is clear that the overall retention probably was only 1% or less of the dose. Durbin et al. (114) and Lucis et al. (115) studied the metabolism of ^{109}Cd administered to rats orally. The results of both these experiments indicated low excretion rates and storage

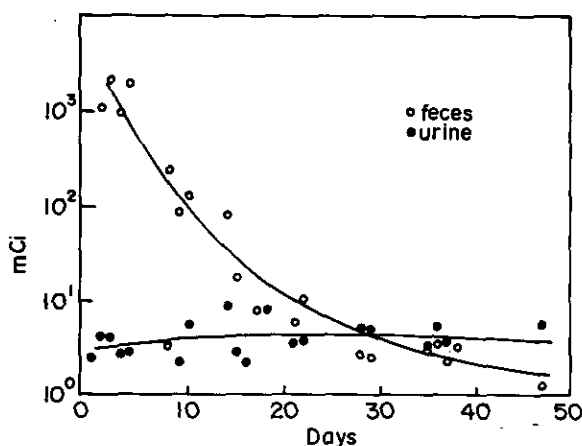


FIGURE 6. Daily excretion of ^{115}mCd in feces and urine (average of 5 subjects). Data of Rahola et al. (111).

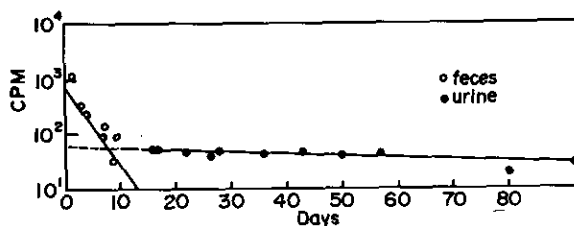


FIGURE 7. Whole-body retention by an individual subject of ^{115}mCd resulting from a single oral dose of cadmium. Data of Rahola et al. (111).

mainly in the liver and kidney. Friberg et al. (30) have also reported that monkeys retained only about 3% of an ingested dose 10 days after ingestion.

Another method of estimating absorption in humans is to determine body burden at autopsy and estimate total intake over a lifetime. Though subject to many errors, such calculations are compatible with an absorption rate of about 3–8% (30).

Although it is quite evident from its acute and chronic effect in occupational studies that cadmium is absorbed from the human respiratory tract, the precise degree and conditions governing pulmonary deposition, clearance, and absorption are unknown. Perhaps the earliest indication of respiratory absorption came from a report by Stephens (116) in 1920. A 67-year-old man who had worked in a zinc smelter for many years was alleged to have had lead poisoning, but his symptoms were atypical. At autopsy, no lead was found in the liver, but 120 ppm Cd and similar amounts of zinc were present. Eight other similar cases were noted. Subsequent studies of autopsy material from persons with occupational exposure by Friberg (117), Kazantizis, et al. (118), Bonnell (119), and Smith, et al. (120) showed both liver and kidneys to have higher concentrations than normal. Lung concentrations were also higher, especially when the exposure was to insoluble pigments (118). Increased blood and urine levels have also been noted in exposed workers (30), but the relation to exposure and pulmonary uptake or deposition cannot be determined.

Generalizations concerning the retention of inhaled cadmium are difficult to make because of the likely variations in range of particle size and solubilities of cadmium compounds from different atmospheric sources. There is strong evidence that cigarette smoking contributes substantially to the cadmium body burden of smokers (121, 122). Rough calculations suggest that the retention of cadmium inhaled in cigarette smoke is substantial. The following calculations lead to such a conclusion.

The body burden of cadmium due to cig-

arette smoking 0.36 mg/pack-yr (where 1 pack-yr denotes one pack smoked per day for one year) is estimated from the data of Lewis et al. (121, 122). On estimating that the sum of cadmium in liver, kidney, and lungs attributable to cigarette smoking is 25 mg/100 pack-yr minus 7 mg from other sources or 18 mg, the total body burden is assumed to be twice the burden in these organs, yielding $(18 \text{ mg} \times 2)/100 \text{ pack-yr}$, or 360 $\mu\text{g}/\text{pack-yr}$. The finding (123) that approximately 2 μg Cd is inhaled per pack leads to a finding that 1 pack-yr provides 730 μg Cd inhaled ($2 \times 365 = \text{one pack smoked per day for one year}$). From these data, the percentage retention of Cd may be estimated:

$$< \% \text{ Retention} = (360/730) \times 100 = 49\%$$

In industry the major hazard from cadmium is from inhaling cadmium oxide fumes. These are probably particles having mass median diameters of 0.5 μ or less. Cadmium oxide also is classed as being very poorly soluble. Using the International Commission on Radiological Protection (ICRP) lung model (124), one would expect roughly 40% deposition and less than 10% retention of inhaled fume particles, mainly because of predicted retrograde movement of particles to the pharynx with ultimate swallowing. There is no experimental confirmation reported for the specific case of cadmium oxide. Thus, the fate of inhaled cadmium is poorly known. In any event, ambient air is only a minor source of cadmium intake for the general population, cigarette smokers expected.

Estimates of cadmium retention in animals have been made. Prodan (125) studied the accumulation of cadmium in cats exposed to the fume, oxide, and sulfide for short periods. The largest percentages were found in the lungs, liver, and kidney. Prodan estimated the retention to vary from about 17 to 30%. In the case of the sulfide exposure, virtually all of the cadmium was found in the lung. Friberg (117) exposed rabbits to a mixture of cadmium and iron oxide dust and found the principal amounts in the lung, liver, and kidney and an es-

timated pulmonary absorption of about 30%.

Little attention has been given to skin absorption. Skog and Walberg (126) applied a $^{115}\text{CdCl}_2$ isotope to guinea pig skin and found 1.8% absorbed in 5 hr. It seems likely that skin absorption is relatively insignificant.

The various studies (30, 127) on absorption and distribution after parenteral injection will not be reviewed here. Cadmium is absorbed well from the injection sites and, again, seems to be stored mainly in the liver and kidney.

The exact mechanism by which cadmium is transported through intestinal mucosa is unknown although there has been some speculation that it may involve mechanisms similar to those of copper and iron transport. There now is substantial evidence that once it reaches the liver its presence stimulates the formation of an unusual protein of low molecular weight, discovered by Margoshes and Vallee (128) in 1957 and named metallothionein. It was originally found in equine kidney, but now is known to be present in the liver and kidney of many mammalian species. It usually contains about equal molar concentrations of Cd and Zn and has a molecular weight of about 10,500. It may contain as much as 5.9% Cd and also has the ability to bind mercury.

Recent work by Nordberg et al. (129) has resulted in the finding of 60% of ^{109}Cd attached to a similar protein in mouse blood after repeated subcutaneous injections over a 6-month period. The protein was attached to the red cell, but clearly separable from hemoglobin. The plasma levels were too low to allow separation and identification of the binding protein. Some portion of plasma binding was thought to be on a low molecular weight protein. This fraction may be filtered in the glomerulus and thus perhaps represents the pathways for tubular reabsorption, storage, and urinary excretion.

The excretion of cadmium in the urine has been reported to be approximately 1–2 $\mu\text{g}/\text{day}$ in the general adult population (130–132). Little is known concerning the relative

importance of urinary and fecal excretion in man. The only study that provides any information indicates that 30 days following oral administration of an oral dose of ^{115}Cd , the rate of fecal excretion was approximately half the rate of urinary excretion (111). There also is some evidence for excretion through the intestinal tract into the feces following parenteral injection in rats (112). In man there is a slight but statistically significant increase in cadmium excretion in the urine with age (130). No correlation with arterial pressure was found.

Hair normally contains about 1 or 2 ppm Cd (30). Although it is possible that this level may vary somewhat with exposure or intake, it does not seem to be a quantitatively important route of excretion. Attempts have been made to correlate hair levels with environmental exposure, but more work appears to be needed to evaluate the technique.

The levels of cadmium in blood and certain organs in the general population appear to be fairly well established and have been reviewed in detail (13, 30). Some of the values for blood, liver, and kidney (30, 132–136) are given in Table 27. The correlation between the concentration in blood and other organs has not been established for man. Thus, blood cadmium has not as yet been shown to be a reliable index of exposure. Concentrations in other organs are considerably lower than in either liver or kidney.

The body burden of Cd in an adult is estimated to be about 30 mg. The newborn is said to contain only about 1 μg of Cd, so there is a gradual increase with age. Of the total body burden, 50–75% will be in the liver and kidneys, about one-third of it in the kidney. Normally the kidney concentrations are 5–20 times those of liver. This may not be the case, however, in exposed persons. From the scattered data collected thus far, it would appear that the estimated body burden in humans varies with age from virtually zero in the newborn to a maximum of 10–18 mg in adults (30). Autopsy data suggest that this maximum is attained in middle life. There is some evi-

Table 27. Average cadmium levels in blood, liver, and kidney of normal humans.

Blood Cd, $\mu\text{g}/100\text{ ml}$	Liver Cd, ppm wet weight	Kidney Cd, ppm wet weight	Reference
1.8			(134)
0.8			(132)
	2	11	(135)
	3	50 *	(136)
0.5	2	22	(30)

* Cortex.

dence that the kidney levels may decrease slightly after that. Friberg (30) has speculated that there may be some loss from the kidney in older age groups but an alternate possible explanation is proposed by Hammer et al. (137), suggesting that the present older generation may have had lower exposures during their lifetime than the current younger generation. The fact that cadmium accumulates to a large extent in the liver and kidney is better established than the range of total body burden and its variation with age.

The concentration of cadmium in the kidneys is of special interest. Industrial experience suggests that the kidneys are especially sensitive to the toxic effects of cadmium. Comparison of data from various sources is complicated by the fact that some report concentrations in outer cortex and others report values for whole kidney tissue. The approximate concentration ratio cortex/medulla is 2.

The threshold concentration of cadmium in kidney above which renal damage is likely to occur is estimated to be 200 ppm in outer cortex (30). This is approximately four times the concentration reported for adults in the general population in one study (136) and about six times the concentration reported for the category of moderate smokers of advanced age in another study (122). The margin of difference might be considerably smaller for moderate smokers in middle age, since the concentration of cadmium is known to fall in advanced age.

Normal Human Intake of Cadmium from Environmental Sources

The principal source of cadmium would

Table 28. Cadmium in various classes of foodstuffs.

Class of Food	Mean concentration, ppm wet weight
Seafood	0.79 (oysters excluded)
"	0.33 (oysters and anchovies excluded)
Meats	0.88
Dairy Products	0.27
Cereals and grains	0.19
Vegetables (legumes)	0.03
Vegetables (tubers)	0.07
Vegetables (leafy)	0.13
Oils and Fats	0.83
Nuts	0.05
Fruits	0.04
Milk	0.025 (median)

appear to be from food rather than air or water. (This may not be true in smokers.) Cadmium occurs in small amounts in all foods used by man or animals although little is known about its chemical form or binding. Table 28 presents some data by Schroeder et al. (50) and Pinkerton et al. (138).

Friberg et al. (30) have reviewed data on cadmium in food in various countries, and there seems to be some general agreement that food averages about 0.05 ppm Cd (wet weight) with, of course, wide variations depending on the source.

There have been relatively few comprehensive studies of the total human intake via foods, but the available data would put the average of 50 $\mu\text{g}/\text{day}$ or less with considerable variation. The best estimates of the U.S. food intake are by Schroeder and Balassa (136), Murthy et al. (139), and Duggan and Lipscomb (140) (Table 29). Further evidence of the approximate correctness of the figure of 50 $\mu\text{g}/\text{day}$ is provided by data on daily fecal excretion of cadmium in the general population. Thus, Tsuchiya (141) reported that daily fecal excretion in four nonoccupationally exposed men was 57 μg , and Essing et al. (142) reported daily fecal excretion to be 31 μg .

Two studies of water supplies would indicate that except for unusual instances of contamination, the intake via water is probably negligible (143, 144). Table 30 summarizes data from the latter study on com-

Table 29. Intake of cadmium from food in U.S.

Intake, $\mu\text{g/day}$ (mean or range)	Analytical method	Source of food	Reference
4-60	Dithizone	Random selection	(136)
27-64 *	Atomic absorption	Institutional diets of children	(139)
26		"Market Basket" survey	(140)

* Range of average values.

munity water supplies. The average intake from drinking water is about 1 or 2 $\mu\text{g/day}$. Little seems to be known as to the contribution of particulate content of water to the total cadmium content.

Airborne particulates or aerosols provide an additional source of Cd to the body. A large amount of data from 35 stations gave an average airborne Cd concentration (145) of 0.002 $\mu\text{g}/\text{m}^3$. There was considerable variation, and Kneip et al. (27) found higher levels in urban air than in suburban air. For example, lower Manhattan averaged 0.023 $\mu\text{g}/\text{m}^3$ while suburban areas were 0.003 $\mu\text{g}/\text{m}^3$. Lee et al. (28) studied the particle size distribution of metals in urban air, using cascade impactors. The mass median diameter was 3.1 μ in Cincinnati, at a concentration of 0.08 $\mu\text{g}/\text{m}^3$. In suburban Fairfax, the concentration of cadmium was lower (0.02 $\mu\text{g}/\text{m}^3$), and the mass median diameter was about 10 μ . The mass median diameter for cadmium seems to have been considerably larger than those measured for lead and chromium in the same areas. On the average, the intake would seem very low, probably not more than a few micrograms per day.

Table 30. Frequency of occurrence and levels of cadmium in drinking water supplies.*

Concentration, $\mu\text{g}/\text{L}$.	Frequency, no. of samples
0-1	962
2-3	782
4-5	655
6-7	129
8-9	38
10-14	25
15-30	4
Total	2595

* Data of Community Water Supply Study, Cincinnati (144).

However, recent work by Lewis et al. on cigarette smoking as a source of cadmium (121) suggests that this may be an important item. Autopsies were performed on 172 adults, including 45 male smokers, whose approximate cigarette consumption was known, and 23 nonsmoking males. The mean age at death for each group was 60 years. Cadmium levels in lungs, liver, and kidney were determined by using atomic absorption. The estimated body burden of cadmium in nonsmokers averaged 6.63 mg and was about double, 15.8 mg, in the smokers. Lewis et al. estimate that their data point to a nonsmoker retention of 1 μg or less per day compared with about 2.5 μg per day for smokers. Estimates of total body burden from the data would give nonsmokers about 12 mg and smokers about 30 mg at age 60.

Szadkowski, Schulze, et al. (146) reported that about 1.4 μg Cd was found in a cigarette and estimated that 0.1 μg Cd per cigarette would be in the particulate phase, 0.03 μg Cd in the gaseous phase. About 0.1-0.13 μg might therefore be inhaled per cigarette. The respiratory intake from two packs per day would be about 4-6 μg , or 10-20 times the intake from reported levels in the air of lower Manhattan.

Menden et al. (123) also estimated that the amount of cadmium inhaled from mainstream smoke was about 0.1 μg per cigarette. They point out, however, that the sidestream smoke contains considerably more total cadmium than the mainstream smoke. It is difficult to estimate how much sidestream smoke is inhaled by the smoker or by others in his vicinity. The figure is no doubt quite variable, depending on whether the smoker and others are out of doors or are in an enclosed room.

The amount of cadmium in dustfall in 77 midwestern cities has been presented by Hunt et al. (147). The geometric means varied from 0.040 mg/m² per month in residential areas to 0.075 mgm/m² per month in industrial areas. These levels would not appear to contribute significantly to human intake via soil or water contamination. However, localized increases are found in some studies in the vicinity of cadmium-emitting metallurgical operations (30).

In summary, it can be stated that the intake for man under ordinary circumstances is principally from food, and most estimates would put this at about 20–50 µg/day. Due to poor absorption from the intestinal tract, it is probable that only about 2 µg/day or less actually is assimilated (0.06×35 µg). The intake from drinking water is presumably 1 or 2 µg/day on the average; due to poor absorption, probably only about 0.1 µg/day is assimilated. The intake from ambient air is also probably very low. Assuming 0.003 µg Cd/m³, 40% retention of inhaled cadmium, and the inhalation of 18m³ of air per day, the daily assimilation of cadmium from ambient air would be approximately 0.02 µg. Air would not be a significant source of cadmium even at the levels reported for lower Manhattan (0.023 µg/m³).

For the nonsmoking, nonindustrially exposed U.S. adult, the likely daily assimilation can be summarized as follows: from air, 0.02 µg; from food, 2.0 µg; from water, 0.1 µg, for a total of 2.12 µg.

This value approximates the reported daily excretion of cadmium, suggesting that adults in the general population are approximately in cadmium balance. This conclusion may be unwarranted, because available data on urinary excretion of cadmium do not distinguish between smokers and nonsmokers, whereas the estimate of daily assimilation for smokers and nonsmokers combined is probably appreciably higher than 2.12 µg and, therefore, probably higher than urinary excretion or perhaps even than urinary and fecal excretion combined.

Toxic Effects in Man and Animals

There are a number of well documented

acute and chronic effects of cadmium in man and animal studies indicate a variety of toxic effects, the significance of which has not yet been demonstrated for man. Many animal experiments have been carried out using relatively large doses parenterally, but because of specific interest in some aspect of cadmium metabolism or toxicity, many of these experiments shed little light on potential, low-level environmental effects.

Effects in Man: The effects in man can be classified as follows: acute oral, chronic oral, acute inhalation, and chronic inhalation effects. The acute oral effects are similar to those of zinc, and there have been many well documented epidemics of acute gastroenteritis from the ingestion of acid-type foods that have been stored in cadmium-lined containers (148, 149). The dose causing the symptoms has been estimated (150) to be as low as 15–30 mg. The symptoms come on almost instantly after ingestion of the contaminated food, and the acute nausea and vomiting may in some cases be followed by a severe gastroenteritis. The actual oral lethal dose in man has not been established, but estimates have been made that it is probably in the neighborhood of several hundred milligrams (150).

As far as is known at present, no chronic toxic effects (except for a Japanese incident) have ever been reported from the oral ingestion of cadmium by human subjects. It is of course possible that some of the chronic toxic effects by inhalation may have been due to swallowing of material being cleared from the lung.

The second important acute toxic effect in man is that of acute pulmonary edema induced by inhalation of metallic fumes or cadmium oxide dust (13, 30). It has been estimated that fatalities have occurred from a 5 hr exposure at about 8 mg/m³ although in one instance recovery was reported after exposure to 11 mg/m³ for 2 hr. In one brief account of a few intermittent exposures to cadmium fumes during silver soldering, a nonfatal acute pneumonitis was noted at concentrations estimated to have varied be-

tween 0.5 and 2.5 mg/m³ over a 3-day period (151).

The acute pulmonary changes seen in man have been reproduced in experimental animals (129). Evidence does not indicate that acute renal injury is a part of the picture of acute inhalation toxicity with cadmium, nor is it known whether repeated acute exposures would subsequently result in chronic renal or lung injury.

The chronic exposure to cadmium through the respiratory tract produces a number of toxic effects, the most important of which is the chronic emphysema first described in the classical report by Friberg (117). Along with the emphysema, a peculiar renal disturbance has been noted, with excretion of relatively low molecular weight proteins in the urine together with some increase in amino acids and at times glucose and calcium. These findings have now been confirmed in a number of other publications and have been reviewed in detail by Friberg et al. (30). Among the more important of these studies are those by Kazantzis et al. (118, 152) Bonnell (119), Smith et al. (120, 153), Piscator (154, 155), and Princi (156).

It is apparent that chronic cadmium emphysema appears only after a period of exposure averaging about 20 years. It was not possible in most of these studies to arrive at the exact exposure levels since in some cases these may have occurred many years previously. However, from Friberg's initial study it would appear that exposure to cadmium oxide dust at levels of about 3–15 mg/m³ may have been principally responsible. In a more recent study (157) of 11 subjects (eight of whom were smokers) exposed to cadmium oxide in the course of extracting cadmium from master alloys, no physiologic disturbances compatible with emphysema were noticed in the group. However, the length of exposure varied between 7 and 11 years, and the air concentrations were lower than those described in Friberg's original work (1.21–2.70 mg CdO/m³). Elevated excretions of cadmium in the urine were noted, varying from about 3 to 65 µg/24 hr. Although this

study included an extremely thorough analysis of all aspects of respiratory function, it is unfortunate that no renal function or urinary protein levels were determined.

The renal effects have been particularly thoroughly studied by Kazantzis et al. (118), by Piscator (154, 155), and by Smith et al. (120, 153). From autopsy material it appears that the principal lesions were in the tubules, but in general the anatomical lesions were not very pronounced except in the most severe cases.

Kazantzis measured cadmium in the lung, liver, and kidney of one case (152) and compared it with data presented by Bonnell (119), Friberg (30), and Smith et al. (120, 153). It is of interest that these combined data on these heavily exposed individuals indicated that the concentrations in the liver might actually have been higher than those in the kidneys and somewhat in contrast to normal individuals.

Another finding of interest in the Kazantzis work is that there was evidence in some individuals of increased output of calcium in the urine.

There may also have been some increase in incidence of renal stones in those with long exposure. Ahlmark et al. (158) also reported a high incidence of renal stones with long exposure to cadmium dust. Nicaud et al. (159) described x-ray changes characteristic of pseudo fractures in certain workers exposed to cadmium oxide dust. Findings of this type were not noted in later studies made by Friberg. Kennedy (160) studied serum calcium levels in rabbits given repeated injections of cadmium. There was a very slight fall in serum calcium which was interpreted as being due to possibly increased renal excretion.

The nature of the protein in the urine has been the subject of a number of studies, particularly by Piscator and his associates (154, 155). Electrophoresis separations show that these have a molecular weight of about 20,000 to 30,000 and that they consist mainly of low molecular weight globulins. Some albumins may be present in minor quantities and these are sometimes

called minialbumins. There may be some increased excretion also of amino acids but, in general, the renal disability is not particularly severe. The renal changes, however, usually precede the development of emphysema and the proteinuria is usually accompanied by an increased cadmium output from the kidney. Friberg (30) interprets this as being due to renal damage.

The form in which cadmium is excreted in the urine is not known although it is possible that it may be in the form of a metallothionein complex.

Slight anemia has been noted in some subjects and it is thought possible that this might be related in some way to interference with zinc, copper, or iron metabolism. At present no explanation is available for the production of anemia. Anosmia has been reported in a group of alkaline battery workmen who were exposed to both cadmium and nickel dust (161).

In 1955 a somewhat unique disease was described in the vicinity of a mine in Toyama prefecture, Japan. The disease was epidemic among elderly women who had borne many children (average of 6). The outstanding features of the disease were lumbar pain and myalgia, spontaneous fractures with skeletal deformation. Pain was readily elicited from pressure applied to bones. Extensive epidemiological studies were instituted after it was demonstrated that the water, rice, and fish in the endemic area were found to contain high concentrations of cadmium and other metals, probably due to contamination of the local river by the effluent from a zinc-lead-cadmium smelter. These studies continue and have been extended to include other areas in Japan where similar mining operations exist. The results of these investigations have been summarized by Friberg et al. (30, 162).

The evidence available to date strongly indicates that this syndrome, termed itai-itai, is due to long-term cadmium exposure. It is the first likely instance of cadmium poisoning in man due to general environmental contamination. The characteristics skeletal changes found in the older women

are not usually observed in industrial cadmium poisoning. They are ascribed to the interplay of cadmium exposure and certain other factors not usually encountered in industrially exposed groups, such as old age, low nutritional status, and multiparous motherhood. The neuromuscular signs and skeletal defects described in itai-itai, however, have also been observed in a series of cases of cadmium poisoning in France during World War II. Four women and two men were affected. All had been exposed for at least 8 years (159). Other cases of this type in industrial cadmium poisoning also have been reported (119, 163, 164). Thus, the musculoskeletal features of itai-itai are far from unique as manifestations of excessive cadmium exposure.

Itai-itai is not solely a musculoskeletal disease. It is accompanied by the more classical renal effects of cadmium seen in industrial poisoning. Proteinuria was always found in clinical cases of itai-itai. Glucosuria and aminoaciduria also usually were present (30). Further, the incidence of proteinuria and glucosuria was much higher among older women and men in the endemic area than elsewhere in Toyama Prefecture. The urinary excretion of cadmium also was three times greater among people in the endemic area than in the nonendemic area of Toyama Prefecture. The prevalence of proteinuria and glucosuria was only somewhat greater among women than among men in the endemic area. Thus, while the musculoskeletal manifestations of itai-itai are seen almost exclusively among older women, the renal manifestations do not appear to be sex-related.

It has not been possible to develop from the available data a dose-response curve for itai-itai. Data on dietary intake of cadmium in the endemic area have been available only for recent years. The recent daily oral intake has been estimated to be 600 μg , ten times the estimated intake for the general population in Japan (165). It seems likely that exposure of that order or higher occurred for at least 20 years and that such long-term exposure may have been neces-

sary to attain the recent incidence of proteinuria among older women in the endemic area. Women born in another area but residing in the endemic area for 20 years or more have an incidence of proteinuria not quite as great as those born and living in the area all their lives (30). The statistical significance of the difference in the incidence of proteinuria in these two groups has not been reported.

More recent studies conducted in Japan indicate that excessive exposure to cadmium may be more widespread in that country than had been previously thought (162). Unfortunately, due to faulty experimental design, these studies have not provided any significant new information in regard to dose-response relationships.

The possible relation of cadmium to hypertension first proposed by Schroeder et al. (166) and by Perry (167) has been the subject of much discussion. The relationship is based primarily on the fact that some data suggest that humans with essential hypertension have more cadmium and a higher Cd/Zn ratio in their kidneys than those without hypertension. Experimental animals such as rats or rabbits are also reported to develop hypertension following cadmium intake by mouth or by injection. However, no relationship between cadmium levels in the kidney and cardiovascular disease has been found. For example, Morgan (168) determined the cadmium content of liver and kidney tissue from 80 individuals at post-mortem and could find no significant difference between a control group and those with either hypertensive or other types of cardiovascular disease. There was also no significant difference in the cadmium-zinc ratio in these individuals. Szadkowski et al. (130) measured urinary excretion of cadmium in a large series of individuals and could find no relation between hypertension and cadmium excretion in the urine.

Epidemiological studies of people industrially exposed to cadmium do not support the idea that cadmium is a significant factor in hypertension (30). People occupationally exposed to cadmium differ from

those not occupationally exposed in some respects that may invalidate the comparison. As an example, Hammer (137) found no rise in blood pressure in cadmium-exposed workers. As is often the case among workers exposed to cadmium, these men also were exposed to zinc. In view of the fact that zinc antagonizes certain vascular effects of cadmium, concurrent levels of zinc exposure may have an important bearing on the question of hypertension due to cadmium. Further research on this important topic is clearly needed.

Other Effects Demonstrated in Animal Studies: One of the most interesting effects of cadmium in animal studies has been its ability to cause an acute necrosis of the rat testis following either parental injections or relatively large sublethal oral doses. This matter has been reviewed recently (13, 30). Studies by Parizek (169) first established the extraordinary protective effect of zinc treatment against the acute atrophy of the testis resulting from cadmium injections. This has also been studied by Gunn and his coworkers (170). Cysteine and selenium also will protect against the cadmium testicular atrophy. By use of ^{109}Cd , it was shown that none of the protective agents actually lowered the amount of cadmium reaching the testis. In the case of selenium there was actually an increased level of cadmium in the testis. Anatomical studies have demonstrated (171) that in all probability this acute cadmium testicular damage results from a toxic effect on the unique vascular system of the testis.

Because of the well-known effect of cadmium on the testis, a number of investigators have looked at the effect of cadmium on the course of pregnancy and fertility. Most of these studies have been based on cadmium injection. Parizek (172) showed that there could be fairly rapid destruction of the fetal placenta with only slight effects on the maternal placenta. When selenium salts were simultaneously injected, no placental effects could be produced. A teratogenic effect of cadmium has been demonstrated in the hamster (173). This effect was inhibited by zinc.

There is no evidence at present that the testicular effects found by injection in experimental animals are to be found in man. Favino et al. (174) investigated the fertility of ten cadmium workers and could find no evidence of infertility. However, one individual stated that he was impotent and this individual had somewhat low testosterone levels in the blood. Friberg et al. (30) quote Cvetkova (175) as having reported somewhat lower weights in male and female children born to women working in a cadmium accumulator factory with relatively high levels of exposure to cadmium. Obviously many more studies of this sort are necessary before any conclusions can be drawn as to human effects of this type.

Studies of possible carcinogenic effects of cadmium have been primarily in experimental animals. The tumors found mostly have been of the sarcomatous type and have mainly been localized at the site of injection (176-180). In two of these studies metastatic tumors occurred in the regional lymph nodes and in the lungs (179, 180). Interstitial cell neoplasms have been shown to develop in the testes of rats, both after direct injection into the testicle and after subcutaneous administration (181, 182). Long-term feeding of cadmium also has been shown to increase the incidence of neoplasms in rats but not in mice (183-185). Kazantzis (personal communication reported that long-term feeding studies in rats nearing completion have not yet revealed any evidence of carcinogenic activity.

Other studies reviewed by Shubik and Hartwell (186) and studies by Decker et al. (113) and Anwar et al. (187) did not reveal evidence of cadmium-related cancer formation in animals.

In view of the frequent demonstration of a carcinogenic effect in experimental animals, the implications for a carcinogenic effect in man need to be explored thoroughly. Indeed, some limited epidemiological studies have been conducted in industrially-exposed populations. Potts (188) reported a high incidence of cancer among 74 men exposed to cadmium for at least 10 years.

Three of the eight men who died had prostatic cancer and two had other forms of cancer. The incidence of cancer of the prostate was also reported to be high in another study of industrially exposed workers (four cases versus an expected number of 0.58) (189). Malcolm (190) concluded that cadmium does not cause cancer of the prostate in man in spite of the suggestive evidence.

In view of the relatively high concentration of cadmium in cigarette smoke, its possible role in bronchogenic carcinoma has received some consideration (30) but a causal role has not yet been demonstrated.

Finally, one of the most interesting aspects of the cadmium toxicity is the discovery by Terhaar et al. (191) that pretreatment with very small oral doses of cadmium would protect against the effects of subsequent very large or fatal doses of cadmium chloride. Doses as low as 10 $\mu\text{g/kg}$ given orally 24 hr before a subsequent dose of 100 mg/kg completely protected against the massive testicular atrophy. Others have since found similar protective effects of pretreatment with small doses against a variety of lesions (192, 193).

It now seems almost certain that the nature of this remarkable protective effect is due to the induction of metallothionein in the liver by subcutaneous or oral administration as demonstrated by Shaikh and Lucis (194). Metallothionein induction by small doses of cadmium has also been confirmed by others (J. Piotrowski, personal communication). Ability of cadmium to induce the formation of such a specific protein has raised a question as to whether this is not a fundamental protective mechanism against toxicity from this and perhaps certain other metals. Although metallothionein has thus far only been isolated from mammalian tissues, MacLean et al. (195) reported recently on the uptake of $^{109}\text{CdCl}_2$ and of $^{65}\text{ZnCl}_2$ by various microorganisms. The organisms involved were *E. coli*, *Anacystis nidulans*, *Chlorella*, *Crithidia fasciculata*, and *Chondrus crispus*. Under the conditions of this study, these bacteria and algae were all able

Table 31. Some cadmium exposure levels causing toxic effects.

Species	Type of Cd	Route	Concn or dose ^a	Duration	Estimated intake, mg/kg ^b	Type of effect; comments	Reference
Man	Soluble salt	Oral	15-30 mg	One dose	0.2-0.4	Vomiting and abdominal pain.	(13, 30, 150)
"	"	"	?1000 mg	"	14	Vomiting and abdominal pain and shock.	(150)
"	CdO fumes	Inhaled	0.5-2.5	8 hr over 2-3 days	0.07-0.35	Acute pneumonitis with recovery.	(13)
"	"	"	8	5 hr	0.71	Fatal acute pneumonitis.	(30)
"	"	"	1.2-2.7	7-11 yr	0.17-0.39	No pulmonary function changes or other toxic effects.	(157)
"	CdO fume and dust	"	3-15	20 yr	0.4-2.1 per 8-hr day	Emphysema, proteinuria and anemia.	(30)
"	CdS dust + some CdO dust	"	0.04-31	2-23 yr	0.006-4	Yellowing of teeth; no pulmonary effects.	(156)
Rat	CdCl ₂	Drinking water	0.1-10 ppm	1 yr	0.007-0.7 per day	No effect.	(113)
"	"	"	50 ppm	3 months	1.75 per day	Anemia, poor growth, low water intake; sacrificed at 3 mo.	(113)
"	Cd acetate	"	5 ppm	2 yr	0.38 per day	Normal growth; survival less at 23 mo.	(201)
"	CdCl ₂	Diet	16 ppm	100 days	0.8 per day	Bleaching of incisors	(202)
"	CdCl ₂	Diet	31-62 ppm	100 days	1.6-3.1 per day	Poor growth and food intake; anemia; cardiac hypertrophy at 62 ppm.	(202)
"	"	"	125-500 ppm	50-100 days	6.25-25 per day	Same as above plus renal tubular and liver changes at higher levels—some pancreatic atrophy.	(202) (203)
"	"	"	15 ppm	6-12 months	0.8 per day	No effect.	(203)
"	"	"	45-75 ppm	6-12 months	2.25-2.75 per day	Bleaching of incisors; anemia; poor growth.	(203)
"	"	"	135 ppm	<6 months	6.75 per day	Marked anemia; loss of weight and death.	(187)
Dog	"	Drinking water	0.5-2.5 ppm	4 yr	0.01-0.05 per day	No effect.	(187)
"	"	"	5-10 ppm	4 yr	0.1-0.2 per day	Slight increase in renal and liver fat.	(187)

Rat	CdO fumes	Inhaled	10	15 min	0.06	No deaths; particle size 0.3-0.5 μ .	(204)
"	"	"	35	15 min	0.21	7/20 deaths in 7 days	(204)
"	"	"	130	10 min	0.52	24/25 deaths in 7 days	(204)
"	CdCl ₂ "smoke"	Inhaled	8	15 min every 2 wk for 6 mo	0.048 per exposure	0/200 deaths; sacrificed periodically up to 6 mo. after exposure; slight reversible pulmonary fibrosis.	(205)
Mice	CdO fumes	"	44	15 min	0.8	Fatal to 9/10 mice.	(204)
Guinea pigs	"	"	37	17 min	0.33	No deaths in 10 guinea pigs in 7 days.	(204)
"	"	"	292	15 min	2.35	6/10 deaths in 7 days.	(204)
Monkeys	"	"	750	20 min (average)	4.3	15/26 deaths in 28 days.	(204)
Rabbits	"	"	8.4	30 min	0.15	0/10 deaths in 7 days.	(204)
"	"	"	123	30 min	2.2	10/10 deaths in 7 days.	(204)
"	CdO and Fe dust	"	45	4 hr	Ca, 6.4 in 4 hr	Approximate LD ₅₀ -56R; dose range 18-78 mg/m ³ .	(115)
"	"	"	9	3 hr/day, 23 days/mo, for 7 mo	0.8 in 3 hr	2/13 deaths due to acute pneumonia; autopsy showed chronic bronchitis, pulmonary fibrosis and emphysema.	(117)
"	"	"	6.5	3 hr/day, 21 day/mo, for 9 mo	0.6 in 3 hr	No deaths; some chronic bronchitis and less marked emphysema.	(117)
Dog	CdO fumes	"	310	10 min	1.63	2/4 deaths in 14 days.	(204)
"	CdCl ₂ aerosol	"	280-360	30 min	5.6 in 30 min	94/157 fatalities in 1-12 days.	(206)
"	CdO dust, < 3 μ diam.	"	3-7 $x=4$	37 weeks, 6 hr/day, 5 days/week	0.74 per day	Animals followed up to 1 yr after exposure; no fatalities during exposure; 4/10 died later of broncho-pneumonia; no significant findings at autopsy.	(207)
"	CdS dust < 3 μ diam.	"	3-7 $x=4$	30 weeks, 6 hr/day, 5 days/week	0.74 per day	No fatalities; blood, urine and organ levels less than with CdO exposure; no pathological changes.	(207)
Cat	CdO fumes	"	4-18, static exposure	24 hr continuous	1.3 (weighted average)	Salivation and respiratory distress in 12 hr; pulmonary edema at autopsy.	(125)

Table 31. Some cadmium exposure levels causing toxic effects. (continued)

Species	Type of Cd	Route	Concn or dose ^a	Duration	Estimated intake, mg/kg ^b	Type of effect; comments	Reference
"	CdO dust	"	400	20 min	0.53	Delayed respiratory symptoms with recovery; chronic interstitial pneumonia and fatty liver and kidneys 1 month later.	(125)
"	"	"	400	11-30 min; 3 exposures	0.7-1.92 per exposure	No symptoms; 1st and 2nd exposure; respiratory distress on 3rd exposure; chronic pneumonia and fatty infiltration of renal tubules 1 month after 1st exposure.	(125)

^a Units of mg/m³ unless otherwise indicated.

^b Certain assumptions were made in obtaining the estimated intake in mg/kg. For diets, the values by Lehman and Nelson (199) were used to convert ppm to mg/kg for various species. For materials given in drinking water, water intakes used for various species were as follows: rat 40 ml/day, dog 300 ml/day. For conversion of mg/m³ to mg/kg inhaled, minute volumes were used as given by Spector (200). Man was assumed to breathe 1.25 m³/hr. If not given, body weights were assumed to be: mouse, 20 g; rat 250 g; guinea pig, 300 g; rabbit, 1800 g; monkey, 3000 g; cat, 3000 g; man, 70 kg. No attempt was made to correct for absorption or retention.

to extract both cadmium and zinc from the solution. Protein separations indicated that both the zinc and the cadmium were bound to a protein with similar properties to the metallothionein isolated from mammalian tissues. Whether such proteins represent the form of cadmium in plants is unknown but this seems possible. In this regard a recent paper by Neathery et al. (196) indicated a difference in the disposition of zinc fed to animals as a salt compared to naturally-occurring zinc. In this study ^{65}Zn was added to media in which corn plants were grown. Calves that had been placed for a short period on a zinc-deficient diet (2.7 ppm of zinc) were then given ^{65}Zn by capsule in pure form or an equivalent dose of naturally occurring zinc in corn. These studies showed that although the absorption and the fecal excretion of ^{65}Zn were similar, there appeared to be a difference in the soft tissue distribution, especially in tissues metabolically active such as kidney and liver. Similar studies need to be carried out with cadmium, since it is clear from other studies of these workers that ruminants have a strong homeostatic mechanism allowing the absorption of zinc but rejecting that of cadmium.

Efforts thus far to demonstrate some essential role for cadmium have been unsuccessful. However, the apparently nearly universal occurrence of metallothionein or similar proteins containing roughly equal mols of cadmium and zinc and the obvious "evolutionary antiquity" of this type of protein continue to make this an important question. A review (197) of cadmium in the metabolism of albumin suggests that perhaps cadmium ions may play an important physiological role in regulating the biosynthesis of albumin and perhaps other proteins including some enzymes.

Evaluation of Environmental Hazard

One approach to the estimation of environmental hazard to man (198) is to compare known toxic and apparently nontoxic exposure levels in animals and man. Table 31 lists some of the more important studies and attempts to convert exposure levels to

intake in terms of mg/kg (= ppm) for various species. The term intake as used here means the quantity entering the respiratory tract or mouth and does not include any estimate of systemic absorption from either route. It is necessary to evaluate the oral or respiratory hazard separately since the hazardous intake levels may differ. Tables 32 and 33 summarize some of the estimated hazardous intake levels in comparison with estimated average intake levels for man from the environment.

On the basis of these data it could be concluded that the present U.S. average daily intake (assuming a 50–100 μg intake and a 70 kg man) via food and water is some 10–20 fold smaller than the uncertain estimates of Japanese intakes causing human renal damage. It is about 1/380 of the lowest reported level causing minimal adverse effects in rats on lifetime feeding, about 1/70 of the lowest level known to cause very minor or negligible effects in the dog over four years, and about 1/35 of the level in dogs causing no demonstrable effect in four years.

The inhalation intake from ambient air in a nonsmoker (assuming an ambient air level of 0.02 $\mu\text{g}/\text{m}^3$, as in lower Manhattan) would be about 1/130,000 the level causing no pathological changes in dogs breathing CdO or CdS dusts daily for 37 weeks. It is about 1/2600 of the current threshold limit value (TLV) level for CdO fume. Smoking two packs a day has been estimated to give an intake about 10–20 times the ambient air intake. Although we do not know the form of cadmium in ambient air, it seems reasonable to assume it is a CdO or CdS particle.

It would appear that although there is a considerable safety margin for the environmental intake from both air and food, the margin is narrower in the case of food. This is true even if one corrects the values for estimated retention via the two routes. It is also probable that the inhaled concentration levels may play a relatively important part in localized pulmonary effects. This should be borne in mind in evaluating any possible pulmonary effects from cadmium in smokers since the concentration of cadmium in the

Table 32. Hazardous intake levels (by ingestion).

Species	Type of exposure and effect	Estimated intake, mg/kg
Man	Single oral dose of soluble salt causing vomiting	0.2-0.4
Man	Single fatal oral dose of soluble salt	14
Man	Daily ingestion via food and water causing renal(?) damage (Japanese studies)	0.012
Man	Daily ingestion in U.S. food and water causing no apparent harm	0.00071-0.0014
Rat	Daily ingestion in water or diet causing severe growth effects, anemia and liver and renal damage	1-25
Rat	Daily ingestion in water or diet over 1-2 yr causing minimal effects	0.38-0.8
Rat	Daily ingestion in water or diet causing no apparent effects	0.007-0.8
Dog	Daily intake in water over 4 yr causing slight increase in renal and liver fat	0.1-0.2
Dog	Daily intake in water over 4 yr causing no apparent effects	0.01-0.05

smoke is about 10,000 times that in ambient air in cities.

The approach to this problem by Friberg et al. (30) is of interest. The assumption is made that there is a direct relation between the concentration in the target organ and the toxic effect. Using available data for the absorption rate from the gut or lung and the excretory rate in the urine, it is possible to calculate the daily intake required to reach a given level in the kidney in a stated length of time.

Assuming a 5% intestinal absorption, it would be necessary to ingest about 130 μg /day over a period of 50 yr to reach the threshold level of 200 ppm in the renal cortex, or 260 μg /day over 25 yr. In estimating the accumulation of cadmium as a result of inhalation, lung retention was assumed to be 25%. Friberg estimates that inhalation

Table 33. Hazardous intake levels (by inhalation).

Species	Type of exposure and effect	Estimated intake, mg/kg
Man	Acute inhalation of fume with reversible pneumonitis	0.07-0.35
Man	Acute inhalation of fume, fatal	0.71
Man	Exposure to fume and CdO in industry over 20 yr with emphysema, proteinuria, and anemia	0.4-2.1
Man	Exposure to fume in industry 7-11 yr; no pulmonary function or renal changes	0.17-0.39
Man	Exposure to CdS and CdO dust in industry; 2-23 yr with no pulmonary or toxic effects	0.006-4
Man	Exposure to CdO fume in industry, TLV	0.015
Man	Exposure to Cd dusts in industry, TLV	0.030
Man	Intake from ambient air in U.S.	
	Nonsmoker	0.0000057
	Smoker (2 packs/day)	0.000057
Rat	Single exposure to fume causing fatal or severe pneumonitis	0.21-0.52
Rat	Single exposure to fume causing no deaths	0.06
Dog	Single exposure to fume or CdCl ₂ aerosol causing severe or fatal pneumonitis	1.6-5.6
Dog	Daily exposure to CdO and CdS dust for 37 weeks, no pathological changes	0.74
Rabbit	Single exposure to fume causing fatal pneumonitis	2.2
Rabbit	Single exposure to fume causing no deaths	0.15
Rabbit	Single exposure to CdO and Fe dust, LD ₅₀	6.4
Rabbit	Repeated exposure to CdO and Fe dust 3 hr/day causing no deaths but bronchitis	0.6-0.8
Monkey	Single exposure to fume causing fatal pneumonitis	4.3

of air containing as little as $10 \mu\text{g Cd/m}^3$ could result in the accumulation of 200 ppm Cd in the kidney cortex in 15 yr of industrial exposure (8 hr/day, 225 days/yr) even if the daily excretion were 0.01% of the body burden. Again, using the assumptions of 25% lung retention, Friberg et al. (30) have estimated that smoking one pack of cigarettes per day from age 15 to 50 could cause a 30% higher renal cadmium level than in a nonsmoker.

Although the assumptions made seem valid as a working hypothesis, there are a number of uncertainties. First the critical level in the target organ is derived from relatively sparse data on concentrations in human kidneys and on animal data. Secondly, the unusual nature of the cadmium binding protein in the kidney makes it uncertain whether overall Cd levels relate to toxicity or whether other secondary factors are important. Finally, we have little or no information regarding the absorption of the chemical complexes of Cd which exist in food, and analytically valid long-term human balance studies of the sort done by Kehoe (208) on lead are not available.

The induction of metallothionein synthesis in the liver by small doses may be a protective mechanism, but the effects of this on long-term toxicity are not known.

Environmental studies such as those described by Hammer (137) represent another approach. These are difficult and require expert planning. Where possible, some form of biological monitoring of the hazard needs to be a part of such studies, and these may need to be carried out over many years. It is unfortunate that neither cadmium urine or blood levels seem at present to be useful as lead or mercury determinations in prediction of hazard. Research on this matter needs to be continued.

Based on present knowledge, and there are many gaps; there is no solid evidence of a hazard to the general population from cadmium in food, air, or water. Contamination of food and water rather than air would seem to present more of a potential problem. This might not be the case with

smoking or excessive occupational exposures. The increased biochemical, toxicological, and epidemiological programs now underway should give the needed data for the answers to these questions.

Conclusions

This review has been concerned with an evaluation of the known toxic effects in man and of some of the other possible or alleged effects based on studies in experimental animals. Food is generally the most important source of cadmium in the environment, where it occurs in close association with zinc. The average intake from food is probably not more than $60 \mu\text{g/day}$. Drinking water and ambient air contribute relatively little to the daily intake under normal circumstances. Airborne cadmium may become significant because of the probability of a higher percentage of respiratory absorption than of oral absorption. However, to date there is no evidence to suggest that ambient air concentrations of cadmium are presenting a hazard. This may not be true, however, if one considers the rather striking potential increase from cigarette smoking. It is evident that in the future epidemiologic studies will have to be much more carefully planned to rule out incidental effects such as smoking, and they should take into account all the known facts regarding cadmium metabolism and toxicity.

An estimate of the safe daily intake in the diet is at present very difficult because of a lack of appropriate information. This is especially true with regard to the nature of the chemical bond of cadmium in plants and meat and other foods. Predictions of toxic effects are also rendered difficult by the nearly universal occurrence of very much higher levels of zinc in combination with cadmium and the protective effect of zinc against cadmium toxicity.

The question of a buildup in the food chain similar to that seen with mercury compounds has been raised but there are reasons to believe this is unlikely. Fassett (13) has pointed out there are fundamental differences in the electronic structure of cadmi-

um and that of mercury. Mercury is able to form extremely stable carbon-mercury bonds, probably because of the presence of an additional 32 electrons, as compared to cadmium (209). Although alkylcadmium compounds are known, they are extremely unstable and very unlikely to be formed or exist for very long in the natural environment. Furthermore, the methylmercury that is built up in the food chain is virtually completely absorbed from the intestinal tract, whereas the cadmium-protein complexes and other forms of cadmium are absorbed only to a very limited extent. In the unlikely event that an individual were to derive his sole source of protein from liver, kidney, or oysters, it is conceivable that the dietary cadmium intake might become hazardous. Until more is known about the absorption of such compounds, however, speculation is very tenuous. The accidental contamination of water supplies may present a very real hazard as well as that of the ambient air. The new data on smoking deserve a thorough investigation.

The role of metallothionein and its induction by small increases in cadmium intake is imperfectly understood. Cadmium bound as metallothionein may be biologically unavailable. If this is indeed the case, evaluation of the toxicological significance of cadmium levels in tissues (particularly the kidney) will require that the implications of binding as metallothionein be thoroughly explored.

Studies of interactions of metals in regard to absorption, transport, and toxic effects have been relatively few. In the case of cadmium, biological interactions with zinc and calcium have been shown. More studies are needed of interactions in order to provide a deeper understanding of the significance of epidemiological data regarding cadmium concentrations in biological systems. Thus, renal damage may depend not only on the cadmium level in the kidney but also on the concurrent level of zinc or other metals.

More effort must be devoted to definition of the kinetic constants which determine the rate of accumulation of cadmium in sensi-

tive organs as a result of exposure via air, food, and water. The paucity of necessary information in this area was clearly revealed by Friberg (30) in his attempt to specify acceptable levels of long-term air exposure in industry.

There is no evidence to suggest that the general population is in imminent danger of excessive cadmium exposure. However, many people (particularly heavy cigarette smokers) probably have approximately one sixth to one fourth of the minimally toxic concentration of cadmium in their kidneys. This margin of safety may not be adequate since the minimally toxic concentration is estimated on the basis of very limited data. Further, there is a possibility that industrially exposed workers may have an abnormally high incidence of cancer of the prostate. Further research should be done to determine whether cadmium is carcinogenic under any circumstances of human exposure, and further efforts should be made to establish no effect levels for cadmium exposure in man.

Research Recommendations

The accumulation of cadmium among people in the general population is substantial. Knowledge concerning the margin of safety is inadequate. Such knowledge as we have is specifically largely limited to the margin of safety for adverse renal effects. It is estimated that current exposure is about one sixth to one fourth of the level necessary to produce minimal kidney damage. Essentially nothing is known concerning the margin of safety in the general population for other health effects of cadmium.

There is need for research in three general areas: (1) endpoints of toxicity; (2) disposition of cadmium in the body; (3) criteria of exposure.

Endpoints of Toxicity: Although much has already been learned concerning the renal effects of cadmium, present knowledge is still inadequate for the purpose of defining minimal toxic effects and the associated exposure. Proteinuria is currently considered to be the most sensitive index of toxicity.

More information is needed as to minimal exposure levels in man associated with this effect. Further work also should be done to explore the possibility that other renal effects may occur at even lower levels of cadmium exposure, such as effects on maximal tubular transport of organic compounds.

More studies also are needed of the effects of cadmium on pulmonary function, again with the view of searching for effects occurring at relatively low exposure levels.

Since cadmium has been found to be carcinogenic in experimental animals, further efforts should be made to explore the implications of these observations. As an example, it should be established whether or not cadmium enhances the carcinogenicity of benzpyrene in experimental animals. Similarly, further epidemiological studies with industrially exposed and nonindustrially exposed populations should be conducted to establish whether there is any association between cancer and cadmium exposure.

Disposition of Cadmium in the Body: It is essential to know the rate of input of cadmium necessary to attain minimally toxic concentrations in specific target organs. Kinetic studies of cadmium absorption, distribution, excretion, and accumulation are needed. Where possible, studies should be carried out on human volunteers. The technique of radioisotope dilution by use of stable isotopes of cadmium as the tracer is promising for gaining much essential knowledge about cadmium metabolism in man. Since a major concern is with the consequences of long-term accumulation, the influence of age on cadmium kinetics is important. Thus, while the daily rate of cadmium excretion may be 1% of the body load in young adults, it may be 2% in old people. It is also important to gain a better understanding of the factors which determine the biological availability or toxicity of cadmium in the body. The role of metallothionein in this regard needs to be explored. Similarly, the relationship of other metals to cadmium levels in tissues and to cadmium toxicity has not been adequately studied. Thus, reports on the incidence of hyperten-

sion or other presumed effects of cadmium in industrially exposed people may not have much relevance to exposures in the general population because of differences in concurrent exposure to other metals, such as zinc, which influence cadmium toxicity.

Criteria of Exposure: Little is known about the relationship between the concentration of cadmium in readily procured biological samples and the concentration at sites of toxic effect in the body. The low concentrations of cadmium found in urine and blood as found in the range of exposure for the general population pose an analytical problem. More sensitive and precise methods for analysis of cadmium in biological specimens are needed. More effort also should be made to develop alternative approaches to measuring cadmium exposure, such as have been developed for lead exposure.

Cadmium in Plants and Animals

Cadmium in Plants

Cadmium in low concentration is probably a normal constituent of all plant tissue, although it generally is not thought to be an essential micronutrient. The toxicity of cadmium to plants is believed to be much greater than that of zinc, an element with which it is commonly associated (210).

The concentration of cadmium in plant tissue is determined by the inherent ability of a plant species to absorb cadmium, and by the concentration of this element in the plant's environment. Where environmental cadmium levels are low, cadmium concentrations in plant tissue frequently vary more with species than with soil type (211). All soils analyzed in a recent geochemical study of Missouri (212) contained less than 1 ppm cadmium, yet the average cadmium content of ash from stems of hickory (*Carya ovata*) was 24 ppm, whereas the average content of ash from stems of white oak (*Quercus alba*) that grew with the hickory was only 4.3 ppm.

Where cadmium content of soils are higher than background amounts, the cadmium

content of plant tissue tends to increase with increased concentrations of soil cadmium. For example, fescue grass (*Festuca rubra*) was found to contain 0.7 ppm cadmium in dry matter where growing on soil that contained 0.4 ppm cadmium, but contained 40 ppm cadmium where growing on soil that contained 26 ppm cadmium (47).

The cadmium contents of many species of plants reflect above-normal amounts of cadmium that are introduced into the environment both from natural sources, and from cadmium pollution of soils, water, and air. Cadmium from these sources may be absorbed by the plant through roots or leaves, or both, and thus be incorporated into the tissues, or airborne particulate matter containing cadmium may be deposited on the surface of leaves.

Certain peat bogs in Orleans County, New York, are enriched in cadmium by the entrance of ground water from dolomite beds that locally contain abnormal amounts of zinc, cadmium, and some other metals. After these bogs were drained for agricultural use, 15 vegetable samples from soil of the bogs were found to have a mean cadmium content of 0.12 ppm in dry material, with a range in concentration from 0.05 to 0.97 ppm (18).

Samples of cedar (*Juniperus virginiana* L.) from a roadside site in Missouri where the soils were thought to have been contaminated by lead ore from passing ore trucks were reported (213) to contain an average of 9.3 ppm cadmium in the ash from leaf and branch samples, whereas similar samples from trees that grew at the same site but at greater distances from the road contained an average of 2.8 ppm cadmium.

Cadmium pollution of agricultural soils through irrigation water from mine drainage in Japan increased the cadmium content of cereal grains that grew on these soils. The polished rice contained an average of 0.49 ppm cadmium in the dry material, and wheat and barley contained several times as much as the rice (42).

Airborne cadmium that is deposited on soil can be absorbed by a plant and trans-

ported throughout the plant. There is no effective method of removing this cadmium from the plant tissues. Goodman and Roberts (47) reported that if plants grew in areas where only a moderate amount of airborne pollution was present, no significant amount of cadmium could be removed by washing the plant samples, but where extreme pollution prevailed, washing removed as much as 45% of this metal from grass samples. These results suggest that at locations where large amounts of airborne cadmium are present at least part of the total amount found by analysis of these plants occurs in surface deposits.

The area around Helena, Montana, is heavily contaminated by cadmium and other metals from smelter emissions. Miesch and Huffman (41) reported that concentrations of cadmium in the upper 10 cm of soil ranged from an average of 72 ppm at sites two-thirds of a mile from the smelter to 1.6 ppm at sites 7.5 miles from the smelter. The U.S. Environmental Protection Agency (133) summarized cadmium contamination in plants from this area as follows: "Lettuce, carrot, beet, bean, and alfalfa grown in the city of Helena during 1969 had an average cadmium content of 0.7 ppm [in dry plant material]. The concentration in edible portions of unwashed vegetables and crops grown in 1969 within a 4-mile radius of East Helena varied from 0.05 to 10 ppm. Pasture grass, alfalfa, and barley straw contained 0.1 to 10 ppm. Barley, wheat, and oat kernels contained 0.1 to 1.5 ppm. Lettuce and beet maximum concentrations were 3.4 and 2.5 ppm, respectively." Similar data on plants growing near a smelter at Bartlesville, Okla., are given by Cannon and Anderson (49). Burkitt et al. (40) and Little and Martin (214) found, near a smelting works at Avonmouth, England, high concentrations of Pb, Zn, and Cd in soils and plants, the maxima recorded Cd (ppm dry weight) being: grass (*Lolium perenne*) 50, moss (*Eurhynchium praelongum*) 148, lichen (*Parmelia*) 90, washed elm leaves 40.

In studies of contamination from a zinc refinery in Japan, Kobayashi (42) found

Table 34. Estimates of cadmium concentrations in some plants and plant parts.

Plant or plant part	Reported or estimated cadmium concentrations or ranges in concentrations, ppm in dry material	
	Environments presumably having normal cadmium levels	Environments having greater than normal cadmium levels
Marine algae	0.1-1	— ^a
Mosses (bryophytes)	0.7-1.2	8-340
Lichens (fruticose type)	0.1-0.4	1
Grasses	0.03-0.3	0.6-40
Alfalfa	0.02-0.2	0.2-2.4 ^b
Grains		
Corn (<i>Zea mays</i>)	0.1	2
Rice (polished)	— ^a	0.5
Barley, wheat, and oats	0.1-0.5	0.1-1.5 ^a
Vegetables		
Asparagus	— ^a	4
Beet root	0.05	0.24
Cabbage leaves	0.05	6-12
Carrots	<0.35 ^a	8
Chinese cabbage	— ^a	41
Eggplant fruit	— ^a	8
Kale	1	— ^a
Leafy vegetables used as pot herbs or salads	0.3-0.5	3-50
Leeks	— ^a	14
Lettuce	0.3-0.5	4-16
Potatoes	0.05-0.3	6-2
Spinach	0.6-1.2	— ^a
Turnip	— ^a	5
Roots	— ^a	15
Leaves	— ^a	2
Tomatoes	— ^a	2
Trees, deciduous		
Leaves	0.1-2.4	4-17
Stems (branches)	0.1-1.3	0.14-1.5
Trees, coniferous		
Leaves	0.1-0.9	0.05-1
Stems	— ^a	0.03-1.5
Epiphytes (Spanish moss)	0.1	1
Floating aquatic plants (duckweed)	— ^a	17
Marine flowering plant (<i>Zostera marina</i>)	0.23	— ^a

^a No data available.

^b Original data given in wet weight; converted to concentration in dry material by assuming 25% water in original sample.

^a Original data given in wet weight; because the water content of grains is very low, these values were not converted to a dry weight basis.

^a Less than the value stated.

that the concentration of cadmium in mulberry leaves (used for silkworm feed) was inversely proportional to the distance of the mulberry trees from the refinery. At 400 m the dried leaves contained about 17 ppm; at 1000 m, 7 ppm; and at 2500 m, 4 ppm. Control samples of the leaves contained less than 1 ppm cadmium. Approximate cadmium concentrations in vegetables from gardens are given in Table 34.

The effect of roadside contamination by motor vehicles on the cadmium content of grass was reported by Lagerwerff and Specht (15) to diminish with distance from the road. Dry grass samples collected 8 m from the road contained 0.63-1.25 ppm cadmium, whereas those collected 32 m from the road contained 0.25-0.58 ppm. These authors attributed the cadmium in the grass samples to both soil and aerial sources. A similar study by Cannon and Anderson (49) gave 0.1-0.14 ppm Cd, with no increase near the highway.

Mosses and mosslike plants have been used by several investigators as sensors of cadmium pollution. Although plants in this group may not be closely related taxonomically, they share the characteristic of having finely-divided and numerous stems and leaves, resulting in a large surface area per unit volume. For this reason (and perhaps also because of great inherent absorption abilities), they can accumulate large amounts of metals either on the plants, within the tissues, or both.

The cadmium concentration in a moss species (*Hypnum cupressiforme* L.) has been used as an index of airborne cadmium pollution in Sweden. The normal cadmium content of this moss was reported to range from 0.7 to 1.2 ppm in the dry plant. In the center of the Greater Stockholm area it contained as much as 7.5 ppm cadmium (215, 216). Oskarshamn, a city of about 25,000 population, has a storage battery factory

that releases cadmium, chromium, nickel, and lead into the atmosphere.

In a study of airborne pollution in the area around Swansea, Wales, Goodman and Roberts (47) reported that the moss (*Hypnum cupressiforme* L.) contained as much as 9.5 ppm cadmium in dry matter where growing near centers of contamination (the moss could not survive in the areas of heaviest pollution), but only 2.0 ppm where growing in nonpolluted areas. In transplant experiments, samples of this moss contained in nylon mesh bags were suspended from trees at sites receiving various levels of airborne pollution. After 2 weeks of exposure, the cadmium content of the moss samples rose from the background value of 2.0 ppm to 337 ppm at locations of greatest airborne pollution.

A lichen, *Cladonia alpestris* (L.) Rabenh., was sampled as an indicator of cadmium pollution from a recently constructed zinc refinery in Finland (59). The background concentration of cadmium in this plant is 0.1–0.2 ppm in the dry matter, but at locations near the refinery the lichen contained 1 ppm. These investigators stated, "Only six months of operation have increased the cadmium level fivefold at about 1 kilometers' distance from the zinc works, but no increase is yet noticeable at a distance of about four kilometers."

Spanish moss (*Tillandsia usneoides* L.), a flowering plant that somewhat resembles true mosses, was sampled throughout its range in the Atlantic and Gulf coastal plains from North Carolina to Texas in a U.S. Geological Survey study (213). This plant has no roots, and grows as intertwined masses of stems and leaves on the branches of trees and other supports, and obtained all essential nutrients from airborne materials. Analyses of 122 samples showed that the lowest cadmium concentrations (2.0–3.8 ppm in ash) were in samples from nonmetropolitan or rural areas where the amounts of airborne cadmium are expected to be low, whereas the highest cadmium concentrations (20 ppm or more) were in samples from metropolitan areas

that had concentrations of heavy industry and other potential sources of airborne cadmium.

Table 34 summarizes data from the numerous reports of cadmium in plants or plant parts occurring in environments presumed to have the normal low levels of cadmium and in those from environments reported to have greater than normal levels of cadmium. Because most reports gave cadmium concentrations on a dry weight basis but did not give ash weights, the data have been converted to ppm in dry plant material. Some data based on ash weight, but without the ash yield being given, were converted to approximate concentrations in dry weight by assuming a reasonable ash yield for the particular kind of plant tissue that was analyzed. In instances of conflicting data, personal judgment was used in selecting the data to be included.

The values given in Table 34 must be used with caution in evaluating specific problems of cadmium in plants. The categories of plants and plant parts represented in this table were, of necessity, often very broad, and doubtless included certain species or varieties and plant parts whose normal cadmium contents differ greatly from the values given for the category. It should be noted that some of the cadmium values in the table were based on very few samples. Furthermore, for some kinds of plant materials, the cadmium concentrations in the environments where the plants grew were only loosely characterized, or were unknown.

Cadmium in Terrestrial Animals

Table 35 summarizes levels of cadmium in small samples of terrestrial animals analyzed by Schroeder and Balassa (136). With the exception of a few samples which may have been contaminated during processing, levels were generally low in the tissues of domestic animals raised for human consumption, and much higher in wild mammals and birds. Using kidney concentrations for comparison, those in domestic animals were of the order of one tenth of those in the wild animals samples, and of the order of one-

hundredth of those in adult humans. Jaakola et al. (59) reported concentrations of 2.3, 5.5, and 51 ppm (dry weight) in the meat, liver, and kidney of an elk from south Finland. All the data quoted above were derived from very small samples and appear insufficient for statistical comparisons.

Schroeder and Balassa (136) determined cadmium in samples of leaves, twigs, and fruit of various trees used as food by deer. Levels ranged from not found to 0.43 ppm with a median of about 0.17 ppm, i.e., of the same order as the level of cadmium in human diets (see above). The levels of cadmium in the kidneys of deer (Table 35) were similar to those recorded in man in the first decade of life (136). Unfortunately, the ages of the sampled deer were not known, but 1-10 years is a likely range for wild deer, so it seems probable that deer concentrate cadmium at roughly the same rate as man.

Table 36 summarizes levels of cadmium in soil, grass, and in the livers and kidneys of rodents (mostly mice and voles) at various sites in the polluted Helena Valley, Montana (133). With the exception of one group of samples collected within 1/2 mile of the smelter (sites 13, 19, and 20), cadmium levels in the kidneys (1.6-7.7 ppm, wet weight) were in the same range as those in the dried grass (1-7 ppm, dry weight). Cadmium levels in the livers (0.2-2.7 ppm, wet weight)

Table 35. Levels of cadmium in tissues of wild and domestic animals.^{a,b}

	Cd, ppm (wet weight)		
	Muscle	Liver	Kidney
Cattle	0.024	0.16-0.20	0.22-1.00
Pig	0.025	0.10-0.20	0.15-0.60
Lamb	0.015	0.14	0.14
Deer		0.35-0.74	2.10-11.70
Red squirrel		0.80-2.03	7.97-17.35
Rabbit		0.30	3.58
Starling		0.57	1.00
Robin		0.55	2.03
Ruffed Grouse		2.04	51.35

^a Data of Schroeder and Balassa (136).

^b Following Friberg (30), measurements reported by Schroeder et al. (50) and Kropf and Geldmacher v. Mallinckrodt (217) have been excluded.

Table 36. Cadmium levels in soils, grass, and tissues of rodents collected in polluted areas near East Helena, Montana.^a

Trapping sites	Cadmium levels, ppm			
	Soil (dry weight)	Grass (dry weight)	Liver (wet weight)	Kidney (wet weight)
16	—	7	2.4	3.8
2, 3	33	6	1.7	7.7
1, 9	23	—	0.4	2.0
4, 6	22	2	0.5	1.8
17, 18	14	1	0.2	1.6
5, 22	10	5	0.5	2.1
13, 19, 20	8	—	16.0	51.0
23, 24, 25	—	1 ^b	2.7	7.2
7, 8, 26	6	1	2.2	6.0

^a EPA data (133).

^b Alfalfa.

were 3-4 times smaller. However, there is no significant correlation between high levels in soils or grass and high levels in the rodents. The age of the rodents was not known, which is again a confounding factor in assessing the rate of uptake. Rabbits collected in the same area (mostly at station 6) had much higher levels of cadmium than the rodents (3.9-9.1 ppm, wet weight, in the livers; 19-61 ppm, wet weight, in the kidneys). However, in a feeding experiment, rabbits fed on a diet including 50-60% of lettuce from East Helena containing 5-12 ppm (dry weight) of cadmium accumulated no more than 1 ppm (wet weight) in 6 weeks (133). Hence the high levels found in wild rabbits of this area probably represent accumulation over one or more years.

It might be expected that predatory animals would concentrate cadmium to higher levels than herbivorous mammals. However, the only measurement reported for a predatory mammal [0.36 ppm in a coyote kidney (50)] is one of the lowest so far recorded for a wild animal.

Mean cadmium levels in cow's milk sold in various parts of the U.S. varied between 17 and 30 ppb (wet weight) (218). Other investigators have reported lower levels in cow's milk: 1.5-4 ppb in Vermont (U.S.) (136); 9 ppb in Germany (142); 10 ppb in Czechoslovakia (219); 3 ppb in Japan (220). Feeding Holstein cows with 3 g of

Table 37. Concentration of cadmium in sea water, bottom sediments, and marine organisms (ppm, dry weight except for sea water).

	Finland ^a				Irish Sea (1955) ^b		Irish Sea and English Channel (1969-70) ^c	
	Polluted area		Other areas		Mean, ppm	Range, ppm	Mean, ppm	Range, ppm
	Mean, ppm	Range, ppm	Mean, ppm	Range, ppm				
Sea water (ppb)	2.90	0.3-10.2	0.7	0.2-2.3	0.11	0.02-0.25	1.3	0.6-3.0
Sediments	0.86	0.17-1.23	1.2	0.47-1.9				
Crustacea							1.6	
Mollusca					1.5	max. 16.3	12.3	1.2-73
Fish								
Muscle	0.026	0.011-0.021	0.041	0.018-0.062				0-1.5
Kidney	1.52	1.48-1.55	0.95	0.02-1.15				
Guillemots:								
Liver								0.1-13
Kidney								0.2-12

^a Data of Jaakkola et al. (59).

^b Data of Mullin and Riley (53).

^c Data of Holdgate (54).

cadmium daily for 2 weeks resulted in concentrations of cadmium in the milk of less than 100 ppb (221).

Cadmium in Marine Animals

Table 37 summarizes the results of four studies in which cadmium concentrations were measured in several different organisms in the same area. Additional data on levels in marine animals are given in Tables 38 and 39. The cadmium levels summarized in these tables were measured and reported in various ways and are not necessarily quantitatively comparable.

Where data are available on the distribution of cadmium within marine animals, the highest levels have generally been found in the digestive and renal systems. Mullin and Riley (53) found that in mollusca levels of cadmium were generally less than 0.02 ppm in shells, of the order of 1.5 ppm in muscle, and up to 550 ppm in digestive glands and renal organs. Brooks and Rumsby (227) found that in oysters cadmium was strongly concentrated in the gills, visceral mass, and heart. Schroeder and Balassa (136) found that in a lobster levels of cadmium were 14 times higher in the digestive gland than in muscle. Jaakkola et al. (59) found that in pike cadmium levels in the kidney

Table 38. Cadmium levels in marine animals.

	Cd level, ppm, dry weight	Reference
Zooplankton, N. Atlantic	13. ^a	(222)
Sponge, Germany	1.1	(223)
Jellyfish, Germany	11.	(223)
Sea anemone, Germany	0.4	(223)
Holothurian, Germany	2.6	(223)
Echinoderms, Gt. Britain	1.	(53)
Starfish, Germany	1.7	(223)
Starfish, U.S.S.R.	1.1	(56)
Molluscs, Gt. Britain	1.5	(53)
Tunicate, Germany	0.6	(223)
Fish, Germany	3.0	(223)
Oysters, eastern U.S.	0.1-7.8	(136)
Oysters, western U.S.	0.2-2.1	(224)
Clams, eastern U.S.	0.4	(224)
Clams, eastern U.S.	0.19	(136)
Mussels, eastern U.S.	0.15	(136)
Crabmeat, Japan ^b	0.12	(136)
Shrimps, U.S.	0.10	(136)
Lobster (muscle), U.S.	0.12	(136)
Salmon, Alaska ^b	0.017	(136)
Sardines, Norway ^b	0.11	(136)
Tuna, Pacific Ocean ^b	0.06	(136)
Swordfish, U.S.	0.04	(136)
Anchovies, Portugal ^b	0.02	(136)
Herring, Norway ^b	0.03	(136)
Whale meat	0.25-0.4	(220)

^a Estimated from level in ash.

^b Canned.

Table 39. Cadmium levels in tissues of marine birds.*

	Sample size	Cd, ppm dry weight	
		Mean	Range
Brown pelican, Florida			
Liver	5	1.80	1.32-2.39
Breast	5	0.275	0.25-0.32
Bone	5	1.66	1.38-1.66
Brown pelican, California			
Liver	3	4.95	0.62-13.62
Breast	3	0.392	0.24-0.64
Bone	5	1.52	1.08-1.96
Wilson's petrel, Hallett ^b			
Liver	10	20.3±5.8	
Breast	8	3.67±2.14	
Bone	8	0.86±0.35	
Wilson's petrel, Palmer ^b			
Liver	10	20.7±4.9	
Breast	10	3.25±0.97	
Bone	10	1.42±0.42	
Snow petrel, Hallett ^b			
Liver	10	27.7±12.2	
Breast	10	5.57±1.88	
Bone	10	0.88±0.17	
Ashy petrel, California			
Liver	10	53.2±20.5	
Breast	10	8.00±4.52	
Bone	9	1.88±0.85	

* Data of Anderlini et al. (226) and Connors et al. (226).

^b Hallett and Palmer are in the Antarctic. Wilson's petrel from Hallett probably spends the southern winter in the vicinity of New Zealand and Australia; Wilson's petrels from Palmer probably migrate to the North Atlantic; snow petrels remain in the Antarctic throughout the year.

were 20-60 times those in the muscle (Table 37). In marine birds, levels in the liver were much higher than those in muscle or bone (Table 39).

On using levels in the whole body or muscle for comparison, most measurements in invertebrate animals in unpolluted areas fall in the range 0.4-2.6 ppm, dry weight (0.1-0.4 ppm, wet weight) (Table 38). Levels in fish (muscle) were generally considerably lower (less than 0.1 ppm, wet weight) (Tables 37 and 38). However, much higher levels were reported in zooplankton from the North Atlantic [mean 13 ppm, dry weight (220)] and in seabirds from the Antarctic [3-6 ppm, dry weight (225)]. The whales and seabirds are long-lived animals and may have accumulated cadmium over a number

of years, but the mean life of the zooplankton is only of the order of months.

The higher levels in marine organisms listed in Tables 37-39 are generally associated with higher levels in the ambient water, usually the result of pollution. For example, at least three of the groups of seawater samples listed in Table 37 contained considerably more cadmium than the global average suggested earlier in this report, and even the fourth (the 1955 Irish Sea data) probably included some polluted samples. The apparent increase on cadmium levels in the Irish Sea between 1955 and 1969 is probably a reflection of additional pollution (228) and is reflected in higher levels in the sampled molluscs. The high levels in some samples of oysters from the U.S. reported in Table 38 (224) are probably also a reflection of pollution. The fact that cadmium levels in petrels from California are roughly twice as high as those from ecologically equivalent species from the Antarctic (Table 39) may also be the result of pollution (225).

Tables 37 and 38 indicate that marine organisms concentrate cadmium to levels much higher than those in seawater. Concentration factors (ppm in fresh organism/ppm in seawater) appear to be of the order of 6000 for zooplankton [mainly copepods (222)], 10^4 for molluscs, 10^3 for echinoderms and crustacea, and $10-10^3$ for fish. Higher concentration factors—up to 3×10^5 for oysters and 2×10^6 for scallops—have been recorded in laboratory experiments with very low levels of cadmium in water (227) but concentration factors higher than 10^5 have not been recorded in free-living molluscs, even in extreme individuals.

There is little evidence that cadmium is concentrated to a substantial extent in marine food chains. Martin's (222) figure of 6000 for the concentration factor in zooplankton is some seven times those recorded for marine phytoplankton (229). However, levels in plankton-eating birds (petrels) are no higher than those in zooplankton, despite the longevity of the birds (Table 39). Levels in fish are generally lower than those re-

corded in marine invertebrates or even marine plants; levels in predatory fish (tuna and swordfish) are not markedly higher than those in fish low in food chains. Levels in the livers and kidneys of fish-eating birds (guillemots) were only of the order of 10 times those in fish in the same area (54). The only measurements reported for starfish (predators on molluscs) were lower than most measurements reported for molluscs (Table 37 and 38). However, in none of these examples were measurements made on successive species in a food chain.

Cadmium in Fresh-Water Animals

In a survey of 406 fish from 49 waters in New York State (230), 68.5% of the fish contained 0.020 ppm or less (whole body residues, wet weight) and 23.5% contained 0.020–0.100 ppm. Only eight fish contained more than 0.1 ppm cadmium, but these in Hudson River. Somewhat higher levels of cadmium were found in fish from the Adirondack mountain area than elsewhere, probably reflecting higher natural levels of cadmium in the mountain lakes. No association between cadmium level and age was found in a sample of lake trout from Cayuga Lake.

Freshwater mussels samples in Massachusetts contained 1.7–3.7 ppm cadmium, wet weight (Massachusetts Department of Public Health, unpublished data), but the mussels had been transplanted as part of a pesticide monitoring program (P. Palermo, personal communication), and it is not clear whether these relatively high concentrations of cadmium (Tables 37 and 38) reflected background levels of local pollution in the rivers to which they had been transplanted.

Summary

Plants: Cadmium in low concentrations appears to be a normal constituent in all plant tissues. The concentration in the tissue is determined by the inherent ability of a plant species to absorb cadmium and by the cadmium concentration in the environment. Where the cadmium levels in the soils are low, the cadmium contents of plants vary

more with species than with cadmium concentrations of the soils in which they grow. Beyond certain background amounts of cadmium in soils, the cadmium contents of plant tissue tend to increase with increased concentrations of cadmium in the soil.

Airborne cadmium, originating in the emissions from the combustion of hydrocarbons or from certain industrial processes, may enter the soils and be absorbed by plant roots, may be absorbed by the leaves, or may be deposited on the surface of plants in particulate matter, until very high levels of cadmium are accumulated by the plants.

There appears to be no natural means by which cadmium is eliminated from plant tissue, and no cultural practice has been found effective in reducing or preventing the absorption of cadmium.

Animals: Only scattered data are available on levels of cadmium in wild or domestic animals. Except for one study on trout, no data appear to have been published on levels of cadmium in animals of known age.

Among small samples of terrestrial animals, cadmium levels in domestic animals were of the order of 1/10 those recorded in wild animals, and of the order of 1/100 those in adult humans. No clear geographical correlation has been demonstrated between levels in herbivorous animals and levels in vegetation.

In marine animals, the highest concentration of cadmium recorded have been in pelagic zooplankton (13 ppm, dry weight), molluscs (locally up to 73 ppm, wet weight) and plankton-eating birds (20–53 ppm, wet weight, in livers). The highest levels in molluscs and birds appear to reflect human pollution. Invertebrates concentrate cadmium to levels 10^3 – 10^4 or more above those in the ambient water; fish to levels 10 – 10^3 times higher. There is no evidence for concentration of cadmium in marine food chains.

Recommendations

A systematic, planned survey of the distribution of cadmium in natural environ-

ments is required. Data available at the present are fragmented among many reports and cannot be integrated into a uniform format because of differences in analytical procedures, various (or unreported) methods of sampling and preparation, and often poorly-defined samples. Reports should include measurements of moisture content and ash weight of samples, to permit interconversion to wet-weight, dry-weight, and ash-weight measurements.

The survey should be planned to serve three functions: (a) to provide baseline information on the distribution of cadmium in relatively unpolluted systems; (b) to investigate effects of locally high ambient levels of cadmium; (c) to identify locally high concentrations which may present a hazard to sensitive wildlife or the risk of high human intake. The survey should be combined with measurements of cadmium levels in soils and waters to provide information on uptake by plants and animals, and should be combined with controlled studies of uptake and retention.

The survey should be based on a small set of indicator species, preferably widespread, common species representing several types of environment and several trophic levels. For plants, the selection should include grasses, trees, algae, and plants used for human food and feed for domestic animals. For animals, it is important to select species in which the age of collected specimens can be determined, either from anatomical characteristics or previous tagging. A list of possible candidates might include deer, voles, trout, crayfish, mussels, seagulls, and petrels. The list should include at least one terrestrial predator (e.g., domestic cats), one predator on molluscs, and one plankton-feeder.

On the largest scale of sampling, the survey network might include one or two sampling sites per state. This should be supplemented with local studies in areas where significant gradients in ambient levels are known to occur, e.g., near smelters, highways, and polluted estuaries.

Experimental studies of uptake over the lifetime of experimental animals are required

for a number of representative species. At least one food chain study should be made in each of three environments: terrestrial, fresh-water, and marine. Model ecosystems (microcosms) might be the most appropriate systems for these studies.

Field studies and laboratory experiments should be designed to determine the relative effectiveness of airborne and soil-held cadmium in influencing the content of this element in plants; that is, foliar versus root absorption. In addition, the properties of soils that affect uptake of cadmium by plants should be studied, with a view to developing cultural methods for reducing cadmium absorption in food or forage crops.

For convenience and economy, all the above studies could profitably be combined with surveys of other heavy metals.

Ecological Effects

Effects on Plants

Reports of cadmium toxicity symptoms in plants grown under field conditions have not been found. The most complete publication on the toxicity of metallic elements and compounds to plants (231) does not mention cadmium as a possible phytotoxin. A bibliography of references to cadmium in soils and plants up to 1966 (232) includes no references to harmful effects of cadmium on plants. An older, much quoted reference (233) stated, "Very little is known of the effect of cadmium in plants or of its occurrence in soils."

John, Chuah, and Van Laerhoven (48) grew oat plants on soils contaminated by cadmium from a battery smelter, and reported, "Oats grown on the contaminated soils contained very high amounts of cadmium in the roots, with smaller amounts in the above-ground portions. Soil treatments affected the cadmium content of roots significantly, but did not affect the cadmium content of tops."

In the experience of the writer, plants that were found by analysis to contain anomalous concentrations of cadmium in their tissues exhibited no symptoms of injury that

could be attributed to this element. Reports found in the literature on cadmium concentrations in plants make no mention of toxic effects, except a Czechoslovakian paper (210) which stated, "All authors agree that cadmium ions are definitely more poisonous [to plants] than zinc ions," and that doses greater than 160 mg cadmium per plant reduced the inorganic phosphorus content of tobacco, and produced necrotic spots on the leaves. The results are hardly applicable to plants growing under field conditions, because of the high concentrations of cadmium used, and because necrosis was produced only when the cadmium solutions were sprayed on the leaves. The same conclusion applies to the data of John, Van Laerhoven, and Chuah (234), who found that addition of 50 mg cadmium as chloride to 500 g of soil reduced the yields of radish and lettuce.

Effects on Animals

No systematic studies of the effects of environmental levels of cadmium on wild animals have been reported. Kobayashi (42) mentioned without detailed description damage to silkworms feeding on mulberry leaves containing 3–17 ppm cadmium (dry weight). In the Helena Valley, Montana (235), horses were reported to be markedly more susceptible to environmental toxicants than other species of farm animals. Chronically impaired horses had higher concentrations of lead (up to 35 ppm) and cadmium (up to 9 ppm) in their mane hair. One horse that died had very high levels of cadmium and lead in the kidney and liver, but these were not reflected by high levels in the mane (235). Goodman and Roberts (47) reported a similar case in Wales, in which a horse died with lethal levels of both lead and cadmium in the kidneys after feeding on grass and hay containing 7.6–9.9 ppm cadmium (dry weight).

The 24-hr tolerance limits for various fish species under various conditions lie between Cd levels of 0.67 and 88 mg/l. (236). However, Ball (237) found that the toxicity of cadmium to rainbow trout was cumulative,

the 7-day TL_m being as low as 8–10 $\mu\text{g/l}$. Pickering and Gast (238) found adverse effects of chronic exposure to cadmium on the reproduction of fathead minnows: reduced survival of embryos was observed at levels as low as 57 $\mu\text{g/l}$. D. I. Mount (personal communication) reports that similar tests with other species of fish have shown adverse effects of cadmium in reproduction at levels below 10 $\mu\text{g/l}$. Sangalang and O'Halloran (239) report testicular damage in brook trout exposed to cadmium levels of 10 and 25 $\mu\text{g/l}$ (as chloride), and gave evidence from *in vitro* experiments that the damage was associated with alterations in androgen synthesis. The level of 10 $\mu\text{g/l}$ associated with reproductive effects in these experiments overlaps with levels observed in natural waters (63, 64) but it is not clear whether results of experiments in aquarium conditions can be directly extrapolated to the more complex physical and chemical environment of natural waters.

Conclusions

Our ignorance of the effects of cadmium in natural or polluted systems is almost total. There is inadequately documented evidence of toxic effects on horses and silkworms in highly polluted areas. Laboratory tests suggest the possibility of adverse effects on fish reproduction even in lightly polluted areas. Some wild birds have been reported with kidney and liver concentrations near to those suspected of causing adverse effects in man.

On the basis of the scanty data available on the uptake, concentration, and effects of cadmium in natural systems, four main types of effect appear likely to occur, at least locally: (1) direct toxicity to plants and animals in polluted areas, especially near smelters, but also perhaps in areas with high natural levels of cadmium; (2) cumulative toxicity to predatory animals which eat the kidneys of their vertebrate prey (such effects should be sought for additionally in lightly polluted areas such as roadsides); (3) cumulative toxicity to animals which feed regularly on molluscs, such as starfish and seagulls (the possibility should be in-

vestigated that such animals may have evolved biochemical immunity to cadmium toxicity); (4) cumulative toxicity and adverse effects on the reproduction of fish. The data of Ball (237), Mount, and Sangalang and O'Halloran (239), quoted above, suggest that such effects may occur with sensitive species even at natural levels of cadmium in fresh water, or in polluted sea water.

Further investigation is needed of these likely ecological effects. However, they are generally expected to be manifested as rather subtle changes in natural systems, in particular replacement of sensitive species by tolerant species. Hence they may be difficult to detect without large-scale experimentation, and difficult to relate conclusively to cadmium in the presence of other pollutants.

Recommendations

Experimental studies are needed to determine levels of cadmium that are toxic to plants, and to define symptoms of toxicity. This may require only simple experimental designs and limited expenditures to determine that toxic thresholds are too high to have practical agricultural importance.

More information is needed on the toxic thresholds of cadmium in wild animals. At first, the species selected for testing should be those in which adverse effects are already suspected, or those in which very high levels are detected by sampling. Examples are silkworms, horses, grouse, and fish-eating birds. The tests should investigate long-term sublethal effects (e.g. on reproduction) rather than acute or chronic lethal toxicity.

In particular, toxic thresholds for effects on phytoplankton, zooplankton, and fish reproduction should be investigated. These experiments should utilize physical and chemical conditions appropriate to natural environments, rather than pure chemicals in clean, filtered water.

Another approach to the elucidation of possible effects of cadmium in natural systems is to compare species populations and community structure in polluted and unpolluted systems.

One suitable site for such a study would be an area around a smelter with marked gradients in ambient concentrations. These should be related to gradients in biological parameters such as the reproductive rate in voles, or the species composition of soil invertebrate communities. Other suitable comparisons would be between biological indicators in polluted and unpolluted estuaries, or polluted and unpolluted streams in the same area. Where differences are found, the causative influence of cadmium should be verified by experiments in model ecosystems.

Analysis for Traces of Cadmium

Trace concentrations of cadmium can be determined by many methods and there are many volumes devoted to the description of these techniques (e.g., 240-243). Unfortunately, analyses for trace constituents are subject to many complications. A technique desirable for the determination of one element may be unsuitable for another element. The reliability of a method for a given element may vary with the nature of the particular sample being analyzed and with the proportions of the coexisting major and minor elements present. It would be most desirable to have a method of analysis for trace amounts of cadmium that would be sensitive, accurate, simple, reliable, inexpensive, rapid, require small samples, give reproducible results, and be unaffected by the presence of other elements and compounds. Such a method does not yet exist, and we must compromise by using the method most suitable for the type of material studied and the objective of the particular experiment.

Some of the more common methods that can be used to determine trace amounts of cadmium are (1) spectrophotometric colorimetry (dithizone method), (2) emission spectroscopy, (3) atomic absorption, (4) neutron activation, (5) electrochemistry (anodic stripping voltammetry, polarography), (6) spark source mass spectrometry, and (7) isotope dilution. A selection of references to papers in which these methods have been used is given in Table 40.

Table 40. Some examples of cadmium analyses on various materials.

Material	Method	Reference
Granite and diabase rocks	Atomic absorption, mass spectrometry, neutron activation, optical spectrography, polarography, spectrophotometry.	Table 41
Waters	Atomic absorption, spectrophotometry, polarography, stripping voltammetry, x-ray fluorescence.	Table 7
Air	Low-temperature ashing of glass fiber filters, atomic absorption.	(27,28)
	Neutron activation	(32)
	Anodic stripping voltammetry	(29)
Food	Dry ashing, atomic absorption	(139)
Shellfish	Homogenization, wet digestion, atomic absorption	(224)
Blood	Wet ashing, dithizone extraction atomic absorption	(134)
	Dry ashing, dithizone extraction, optical spectrography	(132)
Blood, tissues, and hair	Wet digestion, anodic stripping voltammetry	(244)
Renal tissue	Drying, neutron activation	(236)
	Dry ashing, atomic absorption	(237)
Urine	Dithizone, atomic absorption	Table 42

These methods are briefly summarized below. It is not our purpose to give details of procedures or to discuss the necessary precautions required to obtain representative samples and avoid contamination, which are readily available in standard reference works.

Tables 41 and 42 give an indication of the variation in analytical results obtained by different laboratories on samples of geological and biological material.

Further research on methods is clearly needed. It would be highly desirable also that many more interlaboratory comparisons be made on standard samples. Such samples have been available for some time of geological material, for example, the eight rocks distributed by the U.S. Geological Survey, and several others (256). Until recently, the only standard of biological material has been the kale prepared by H. J. M. Bowen; the new standards prepared by the U.S. National Bureau of Standards of "orchard leaves" and beef liver should be very useful.

Spectrophotometric Colorimetry

The method is based on the measurement of the degree of absorption of light at a given wave length that is characteristic of a specific ion or complex. Thus, the maximum absorption of light by a solution of cadmium dithizonate (the most commonly

Table 41. Cadmium determinations by many methods in U.S. Geological Survey rocks granite G-1 and diabase W-1.

Cd, ppm *		Method ^b	Reference
G-1	W-1		
5±2 *	6±2	Po.	(245)
0.06 (3)	0.33 (4)	NA	(8)
0.05	0.08 (2)	OS	(246)
0.08 (4)	0.30 (4)	Po.	(247)
—	0.3 (3)	Sp.	(247)
—	0.28	Sp.	(248)
<0.3	<0.3	Sp.	(249)
<0.2	<0.2	MS	(250)
—	0.22	Po.	(251)
0.003 (2) *	0.27	NA	(251)
—	0.016 (2) *	Po.	(252)
0.047	0.164	AA	(253)
—	0.155	NA	(254)
0.022	0.151	NA	(255)

* Numbers in parentheses denote the number of determinations.

^b Methods: AA = atomic absorption; MS = mass spectrometry; NA = Neutron activation; OS = Optical spectrography; Po. = polarography; Sp. = spectrophotometry.

* Discarded.

used complex) occurs at the wavelength 518 nm, and the intensity of absorption is related to the concentration of cadmium dithizonate in solution, which can be determined by appropriate calibrations with standard solutions.

Concentration by selective extraction by organic solvents of the cadmium dithizon-

Table 42. Cadmium concentrations in 13 urine samples as determined in five laboratories.^{a,b}

Cd concentrations in urine, $\mu\text{g/l.}$							
Laboratory 1	Laboratory 2		Laboratory 3		Laboratory 4	Laboratory 5	
	2a	2b	3a	3b			
1.	16.6	41.0	12.7	14.6	9.2	12	12.3
2.	16.0	47.0	12.4	18.6	16.8	15	12.0
3.	24.0	0	10.4	9.3	8.4	7	7.3
4.	12.0	6.8	8.9	9.3	8.4	7	6.0
5.	16.0	12.0	14.6	24.8	23.2	18	16.5
6.	190.4	153	150.7	154.8	147.4	182	152.9
7.	53.4	100	48.1	51.6	44.2	47	49.9
8.	173.6	125	138.3	128.3	111.6	148	139.2
9.	68.4	56	55.5	53.2	43.2	48	36.8
10.	39.4	63	38.9	35.5	31.6	41	35.6
11.	5.4	50	2.4	4.5	4.2	6	4.0
12.	128	165	125.8	108.4	105.3	93	136.7
13.	22	26	13.1	12.9	11.8	20	13.2

^a Data of Friberg et al. (30).

^b The following methods were used: Laboratory 1, dithizone method; laboratory 2a, dithizone-atomic absorption; laboratory 2b, dithizone-atomic absorption; laboratory 3a, dithizone-atomic absorption; laboratory 3b, dithizone method; laboratory 4, dithizone-atomic absorption; laboratory 5, dithizone-atomic absorption.

ate complex is a necessary step, which can remove many interfering elements with proper adjustment of pH during the extraction. The method is less sensitive than some of the others, except where concentration is comparatively easy, as for sea water, in which levels of parts per billion can be determined (53).

Special modifications, such as the use of ultraviolet spectrophotometry or fluorometric methods give promise of increased sensitivity of determination of cadmium.

Emission Spectroscopy

When elements are vaporized by means of a spark or an electric arc, the atoms present are energized to excited energy states; return of these energized atoms to the ground state is accompanied by the emission of light, the frequency of which is characteristic of each element. Resolution of these spectral lines and the determination of their intensities serve as the basis for estimating the concentrations of the trace elements present.

The method is most commonly used for direct analysis of solid samples, without pretreatment, because it makes possible the determination of many elements simultan-

ously. The inherent variations due to varying composition of samples, variations of degree of volatility, etc. require careful standardization against known material of similar composition and the use of internal standards. The sensitivity for the direct method (generally 5–10 ppm) is not as good as in most of the methods discussed; it can be improved by concentration methods, followed by spark emission on solutions, or by arc emission of the evaporated dried solids. Such methods have not however, been used extensively.

Atomic Absorption Spectrophotometry

The basic principle of the method is that vaporized elements will absorb radiation of their characteristic frequencies by being activated from the ground energy state to a higher electronic energy state. The concentration of the atomized element is measured by the degree of absorption of its characteristic frequency of light.

Atomic absorption is one of the most widely used methods for determining traces of cadmium, because of its relative simplicity, speed, and sensitivity. It is commonly preceded by a concentration procedure, most often by dithizone extraction, to improve the

sensitivity and to eliminate interferences, especially the serious interference caused by the presence of NaCl; some of the early data on cadmium in biological samples may be seriously in error because this source of error was not then known (30).

Recent modifications of the method, such as atomic fluorescence flame spectrometry (257) and flameless atomic absorption, give promise of lowering sensitivity limits for cadmium to well below 1 ppb Cd (258).

Neutron Activation

Many elements, when subjected to bombardment by neutrons in a reactor, form radioactive isotopes. The amount of a given isotope formed is proportional to the concentration in the original sample of the specific element, the neutron flux used, and the crosssection of the parent nuclide. Instrumental analysis of the energy of radiation and the decay curve is used to identify the desired radioactive isotope, the amount of which is determined by comparison with standards that are irradiated simultaneously with the unknowns and which have been carried through the identical separation and counting procedures (259). Rarely is direct counting possible; usually separations must be made from other radioactive isotopes that might interfere in the final counting procedure. The chemical separations are made after adding a known, generally much larger amount of the nonradioactive element after irradiation is completed. Although such separations may be quite complex, it is unnecessary to make quantitative recoveries of the element sought, because yields can be calculated from a knowledge of the amount of nonradioactive carrier added (250).

The neutron activation method is extremely sensitive. For cadmium the isotope ^{115}Cd is generally measured, with sensitivity in the ppb range if chemical separations are made. The principal disadvantage is the need for a nuclear reactor and a "hot" laboratory.

Electrochemical Methods (Polarography, Anodic Stripping Voltammetry)

The polarographic method is based on the current voltage curves obtained by the elec-

trolysis of solutions under special conditions, using a dropping mercury electrode. With proper choice of electrolyte, it is possible to obtain separate steps in the curves for each element present, the height of each step (current) being proportional to the concentration of the ion, and the location (potential) being dependent on the ion and on the nature of the base electrolyte.

The method in its conventional form can be used to analyze solutions for cadmium at about $10^{-5}M$ concentrations and with special techniques for concentrations down to $10^{-7}M$.

Anodic stripping voltammetry is essentially a polarographic method in which the element is slowly plated out of a small volume of solution on a small electrode (usually mercury-plated graphite) under carefully controlled conditions. After electrolysis is complete, a reversed voltage is applied, causing rapid dissolution of the plated element from the amalgam and thus producing a relatively large signal on the plot of current flow versus voltage.

The method is extremely sensitive and is especially useful for natural waters; its use may yield information on the nature of binding of cations in waters.

Spark Source Mass Spectrometry

Analyses for traces of metals by this method involves the volatilization and ionization of the material being analyzed by applying a radio-frequency spark, followed by measurement of the ions formed by their masses in a high-resolution mass spectrometer. The method is extremely sensitive, permits the simultaneous determination of many elements, and can be used for nearly all types of samples. The main problems are erratic variability of the emissions of ions from a spark source, which requires that an internal standard such as lutetium be used, and the formation of multiply charged ions. Precisions of about $\pm 10\%$ have been reported for rock samples (260); further research should improve this.

Isotope Dilution

The method of stable isotope dilution, ap-

plicable to the determination of traces of any element composed of two or more stable isotopes, is based on the mass spectrometric determination of the proportions of two stable isotopes in a sample to which a known amount has been added of a "spike", i.e., of a sample of known isotopic composition enriched in one of the isotopes that is of low natural abundance (261). The procedure requires the complete solution of the sample, addition of the spike with thorough mixing, separation of the element from possible interfering elements, and determination of the isotopic composition. For cadmium, the spike might be enriched in ^{106}Cd (normal abundance 1.22%) or ^{108}Cd (normal abundance 0.88%) and the ratio measured against ^{112}Cd (24.07%) or ^{114}Cd (28.86%).

The method is extremely sensitive, with very high precision and accuracy. It has the advantage that quantitative recovery in separation is unnecessary; also the yield does not have to be determined, because a ratio, rather than an absolute amount, is measured. Contamination by reagents can be determined by parallel experiments. Although the method has not often been used for cadmium, probably because it is relatively slow and expensive, it is to be considered one of the ultimate means of monitoring faster and less expensive methods.

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